INTERNATIONAL ATOMIC WEIGHTS

1947

Published by the *Journal of the American Chemical Society*

	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	190.2
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	30.98
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.010	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.54	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.2	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulfur	S	16	32.066
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.003	Tellurium	Te	52	127.61
Holmium	Ho	67	164.94	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0080	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.85	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	183.92
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	174.99	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

FUNDAMENTAL CHEMISTRY

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Ajaz. L.L.B Ist year

By HORACE G. DEMING

FUNDAMENTAL CHEMISTRY
INTRODUCTORY COLLEGE CHEMISTRY
GENERAL CHEMISTRY
A LABORATORY MANUAL OF COLLEGE CHEMISTRY

By H. G. DEMING
AND
SAUL B. ARENSON

EXERCISES IN GENERAL CHEMISTRY AND QUALITATIVE ANALYSIS

By SAUL B. ARENSON

CHEMICAL ARITHMETIC

FUNDAMENTAL CHEMISTRY

An Elementary Textbook for College Classes

BY

Horace G. Deming

PROFESSOR OF CHEMISTRY
UNIVERSITY OF NEBRASKA

SECOND EDITION

NEW YORK: JOHN WILEY & SONS, INC.

LONDON: CHAPMAN & HALL, LIMITED

Chemistry

SECOND EDITION
Fourth Printing, April, 1949

PRINTED IN THE UNITED STATES OF AMERICA

Preface to the Second Edition

In this edition the earlier chapters have been simplified in many ways—for example, by presenting the internal structure of atoms in an elementary way in a single chapter, and postponing the details of nuclear chemistry to near the end of the book. Then, when ordinary, extra-nuclear chemistry has been made somewhat familiar, attention is turned to such spectacular recent nuclear achievements as the fission of uranium and plutonium, and the creation of new synthetic elements.

Such typical new developments as silane derivatives, silico-organic compounds, and a number of new inorganic complexes have been introduced, to give the student a hint that inorganic chemistry is not limited to simple acids, bases, and salts. Note has been taken of a few other typical recent accomplishments, such as the development of the sulfa drugs and the production of antibiotics by mass cultivation of microorganisms.

Many new problems and exercises have been included. The use of *dimensions*, in Appendix H and elsewhere, as an aid to solving numerical problems, has been given the prominence that it deserves.

H. G. D.

LINCOLN, Nebraska
November 16, 1946

Preface to the First Edition

This book was made in the classroom. It is the result of an experiment with a class of 240 students, who from the beginning were encouraged to ask questions. The effort was to present chemistry as a *manner of thinking*, rather than as a collection of facts, however systematized, or as an array of unsupported assumptions, to be taken on faith.

If one sweeps away the unrelated details that burden chemical instruction, the most important features of chemistry as a science are easily perceived (see the summary on p. xiii). The problem was to present them in an orderly way, passing gradually from simple to complex phenomena, and guiding our development by actual classroom experience.

Questions asked by students, as the work went forward, were often of an unexpected sort: "If heat is the motion of molecules, what is cold?" "If a reaction absorbs heat, doesn't the material get hotter?" Such queries show how often students miss the whole point of arguments or demonstrations, because of a slight misconception about something simple and fundamental. To know what sorts of trouble students actually are having, and to modify instruction accordingly, have been the guiding principles in the preparation of this book.

The most important point about such a plan is that it introduces no important theory until the student has begun to feel the need for it. The error of piling theory upon theory in the first few weeks of instruction, before any proper background of facts has been acquired, is avoided. To inform students, within the space of a few lectures, that matter is composed of atoms and molecules, that atoms contain central nuclei about which electrons whirl, and that the nuclei themselves contain neutrons and protons, is to be more dogmatic than any churchman. To hand science down as a succession of believe-it-or-not dicta is to miss the chance to disclose how it grew and what is meant by the scientific mode of thought. That forfeited, one may wonder what there is left in science worth teaching at all.

Those who seek unusual approaches in this book may be interested in observing:

1. The absolute scale of temperatures is made to appear logically as a measure of the average exchangeable energy of molecules, instead of being disposed of in an arbitrary way, in terms of an imaginary ideal gas.

2. Energy is given a prominent part to play in all the transformations of matter.

3. A special effort has been made to develop precision in the use of scientific words.

4. Definitions have been made to conform to new points of view.

5. More than common attention is given to what might well be considered the chief concern of chemical science, namely, the question of why chemical substances react at all, and what forces hold atoms together in chemical union.

The result differs from the author's "General Chemistry" not only in manner of approach but also in giving less attention to industrial details. Since it diverges radically in content and treatment from high-school textbooks it should be serviceable in classes in which some of the students have already had a high-school course yet others have not. It differs from the "Introductory College Chemistry" in giving a fuller treatment of principles, with less space devoted to historical matters and less consideration to the cultural possibilities of chemistry, in which chemistry makes contact with other fields of human effort.

H. G. D.

LINCOLN, Nebraska
July 5, 1940

Acknowledgment

In a very real sense the heroes of science are not its discoverers or practitioners, but guinea pigs on whom many of its hopeful ideas are first tried out. So this book is dedicated to the "Guinea Pigs," a group of students not majoring in chemistry, who followed the main class, testing the manuscript page by page, to discover and eliminate ingredients that might be unassimilable or definitely toxic. That they endured this test without being made allergic to chemistry lends hope that others may fare as well. The diet here presented includes a fair proportion of mental vitamins, and any descriptive textbook or a series of amplifying lectures will provide the necessary roughage.

For assistance in outlining a brief course, with minimum requirements, for students not majoring in chemistry, the author is indebted to many teachers and former students who have used his other books. His daughter, Margaret Deming Lund, made her training in the classics contribute to exposition of modern science, remarking that difficult subjects are made easy in proportion as their wording is made clear and precise.

Suggestions for a Briefer Course

The topics presented in the first eight chapters of this book are believed to be fundamental to an elementary course of any type. Thereafter, in many chapters, a choice may be made. Students not majoring in chemistry, who perhaps will have no further courses in the subject, may be limited to topics marked ▶. This will enable them to make rapid progress through the ensuing twelve chapters, and so be brought, at the earliest possible date, to the descriptive chemistry of the individual groups of elements, according to the Periodic Table.

From Chapter 21 onward, at about the beginning of the second semester, the instructor is left to make his own selection of topics, according to his objectives. Historical incidents or industrial applications are but briefly indicated in this book and may need to be developed in supplementary lectures. Whatever the choice of topics, sufficient background will have been furnished by the first eight chapters, plus the topics marked ▶ in the following twelve. The manuscript has been read very carefully to make sure that the abbreviated version really gives adequate preparation for all that comes afterward.

Students who have had a previous course in the high school may be asked to study topics that others omit; or the whole class may be put through the brief course, as far as the end of the first semester. Topics previously omitted may then be included in a review. Another plan is to reserve the highest grades for students who are able to master more than the minimum requirement.

Contents

General Principles

This list is for the convenience of instructor and students, in review. Important principles are introduced in simple form, then gradually developed, as they repeatedly recur, in later chapters.

Chapter 1

THIS CHANGING UNIVERSE

1. Man in the Midst of a Universe of Change

To modern man, as to his primitive ancestors of long ago, the most impressive fact about the material universe is never-ceasing change. Living plants and animals appear upon the earth, grow to maturity, and finally pass from sight, becoming once more a part of the inanimate world from which they sprang. Glaciers creep down mountainsides, crumbling and wearing away the granite cliffs. A lightning flash kindles fire in a forest, and soon the woodland itself, its verdant covering, and the living creatures within its depths have vanished.

Primitive magic and religious ritual had their origin in man's efforts to control events in the material world, thus to secure rainfall, abundant harvests, and good hunting, or to ward off disease and disaster. Yet in spite of all ritual or magic, man shares the fate of the rest of the material universe, changing with each breath he draws, and passing from the earth at last, to leave behind him only evanescent reminders of his life and activities: decaying temples, rusting bridges and armaments, crumbling fabrics, and cities overwhelmed by jungle, flood, or fire, while continents are slowly worn away to the level of the sea, and ocean bottoms uplifted into dry land.

These never-ceasing changes of the material universe, which not only create but also in the end destroy all material *objects* (samples or portions of matter), are possible only because they transform, beyond easy recognition, the very *materials* (different kinds of matter) of which these objects are made. Living plants and animals, for example, owe their brief existence as objects to transformations that convert materials present in the soil and air into those that compose living tissues; and their final disappearance from the earth is due to other changes, involved in the process of decay, which reconvert the materials of which they are made into those of soil and air.

2. The Command over Fire. Fire as a Mystery

Primitive man, nevertheless, learned how to retard or arrest, and hasten or control, many of the changes to which his material surroundings were subject. The most spectacular of his accomplishments was the mastery of fire. This triumph marked the beginning of the long, hard trail that has led upward from savagery to civilization. It was won long before the dawn of history, during a period of time that included one or more of the great ice ages, when glacial sheets, descending from the north, overspread most of the temperate lands now possessed by civilized man. Command over fire helped man to survive in spite of the southward thrust of the great ice sheets. His home was in the depths of caves, where a glowing fire rolled back the curtain of the night, kept wild animals at bay, and provided warmth for all in defiance of ice and snow.

A central place in human interest was won not alone by the utter necessity for the control of fire by man: fire was one of the great mysteries of nature, everywhere to be observed. The beginning and close of each day were marked by the rising and setting of the sun—a ball of flame. Volcanoes poured forth glowing lava, setting fire to whole countrysides. Dry branches of trees, rubbed together by a breeze, sometimes caught fire. Lightning often set forests ablaze. Piles of moist straw frequently smoldered and at length burst into flame. The primitive workman, fashioning arrowheads, observed a shower of sparks when stone hammer fell on flint. Fireflies flitted through the dusk of evening; luminous fish swam in the tropical seas; water broke from paddle blades at night in phosphorescent spray; and meteors flashed across the skies against a background of the stars.

Were these all manifestations of fire? How did fire come to earth? How might humanity avoid its fury and propitiate the gods that controlled it? Numberless myths and legends arose in the attempt to explain this world-wide mystery. Since no one really knew how fire first arrived on earth, nor what happened in burning or in the use of fire in winning metals from their ores, imagination created endless stories to account for these events. Man made use of fire for thousands of years before he began to suspect what really happens in the process of burning. The most he could do was in some degree to control and direct the *transformations* (namely, thorough alterations) that fire induced. He learned that food is rendered palatable by cooking; that clay, strongly heated, surrenders its plasticity and hardens into stone; that certain "earths," strongly heated in the presence of charcoal,

yield useful metals. Fire became mankind's most useful servant, while remaining nature's greatest mystery.

3. The Ancient Chemical Arts

Primitive man very early acquired the skill *to direct and induce* many other transformations of material things. And no wonder!

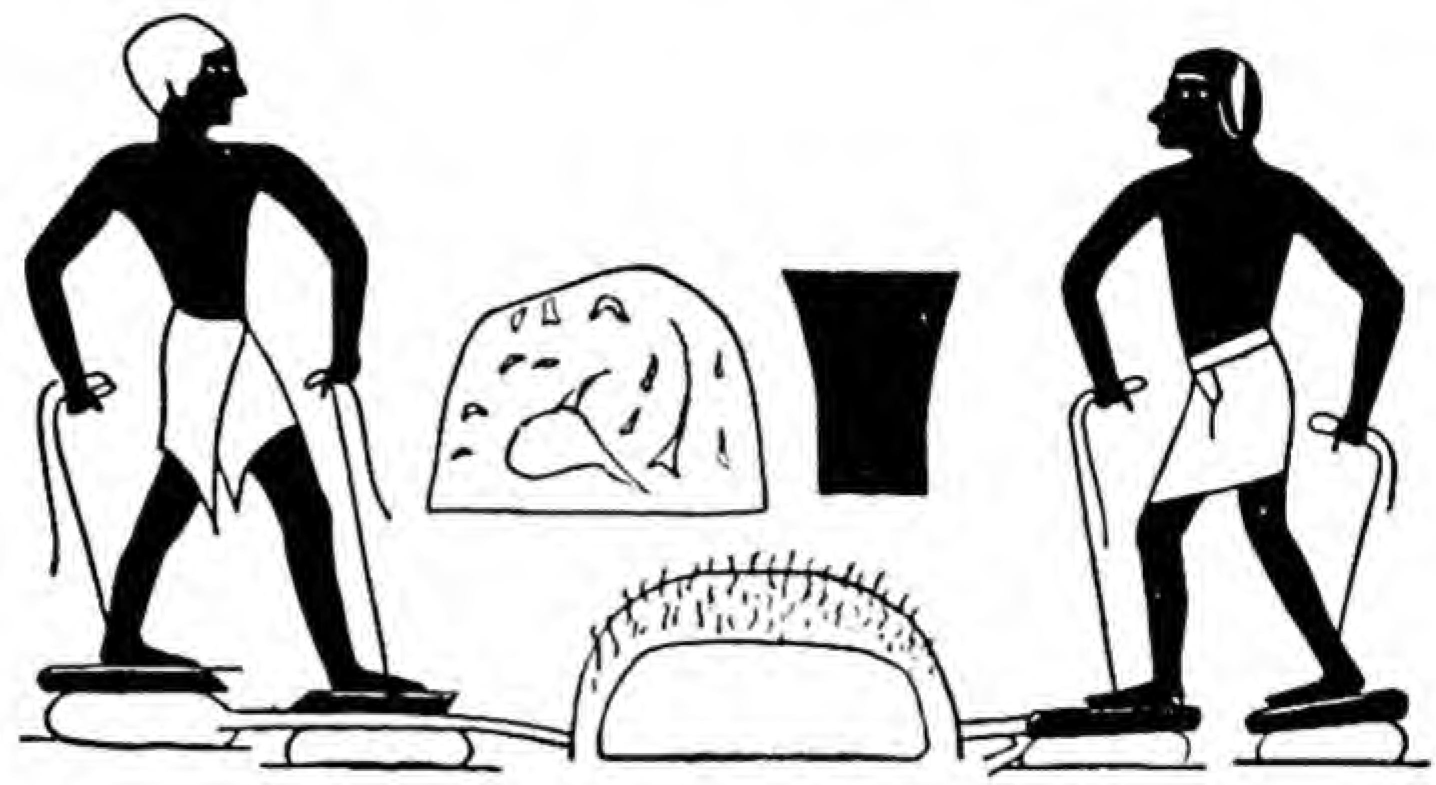


FIG. 1. Production of metals in ancient Egypt. Bellows, worked with the feet, created an air blast. The furnace was a mound of clay, shown in cross section with a crucible.

The very existence of his race depended on gaining a control over nature that was denied the great beasts of jungle, forest, and tundra. A large part of the energies of the human race, down to this very hour, has been devoted to transforming *materials*, to be used in food, clothing, shelter, warfare, or the chase. Only recently in the development of the human race, and to a few of mankind, have come leisure and capacity for preoccupation with non-material things, in brief, for meditative thought.

Courtesy of the American Museum of Natural History, New York

FIG. 2. Prehistoric Mexican ceramic art. The god of games and feasting.

The earliest historical races already employed hundreds of different materials, which they subjected to the most manifold transformations. They tanned leather, prepared and dyed textile fabrics, obtained metals from their ores, prepared medicinal substances from plants and animals, made mortar, enamels, paints, lacquers, and ultimately glass. Later came the discovery of glazed *ceramic products* (those made from clay), metallic alloys, the art of hardening steel, and the hydraulic cement that made possible the Roman aqueducts.

Then porcelain was invented, about a thousand years ago, and paper.

All these discoveries in the practical *arts* of transforming materials are entitled to be called "chemical arts"; yet they were won by forgotten geniuses of the past, through countless unremembered trials and failures, before chemistry as a *science* had begun to take form. Science is a systematic *manner of thinking*, which provides a short cut to results that persistence, continued over many generations, with countless trials and failures, may sometimes obtain without the aid of science.

4. Modern Chemistry Considered as an Art

Modern chemistry, considered as an *art*, has three chief problems:

1. *To identify or distinguish materials.* Many materials can be identified at sight. A glance will usually identify glass, or distinguish copper from iron, or coal from limestone. Nevertheless, when two materials are of the same general appearance more care may be needed to tell one from the other. The first colonists in Virginia wasted their efforts collecting pyrite (fool's gold), a brittle yellow mineral which they mistook for real gold. Its brittleness and relative lightness should have shown them their mistake.

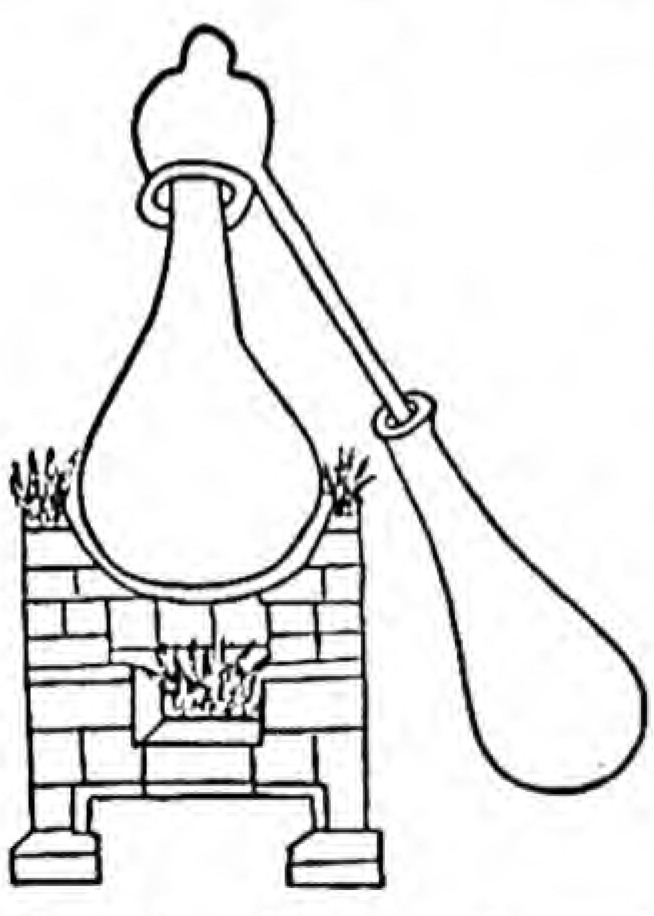


FIG. 3. Preparation of nitric acid (1400 A.D.) by distilling sodium nitrate with sulfuric acid.

Sometimes two materials may be so very much alike that some special test may be necessary to distinguish them. Rayon has often been passed off for silk, and imitation leather for real leather; and we have all heard of wooden "nutmegs" and glass "diamonds."

2. *To separate materials, when they are intermingled or combined with one another.* Often the separation is easy: to separate salt from water, we need only evaporate the water, and the solid salt will be left behind. To separate iron from brass filings, we may take advantage of the fact that iron will cling to a magnet, whereas brass will not.

At other times the separation of materials from one another calls for considerable skill or chemical knowledge. This is especially true when two or more intermingled materials have entered into *chemical union* (an intimate association, in which each of the materials so alters the others that the result is a new material, very different from those

that went into it). Materials that have entered into chemical union are often said to have *combined.*

Thus a red-brown earth called *hematite* really consists of iron in intimate association with oxygen. Hematite is not attracted by a magnet, and no one would guess that it may contain as much as 60 per cent iron. To separate the iron in a form that would be recognized by anyone, it is only necessary to mix the hematite with charcoal and heat the mixture in a current of air.

3. *To determine the means and conditions for transforming materials into materials of other kinds.* Sometimes we are interested in causing or assisting such transformations of materials, as when coal is transformed into ashes and invisible gaseous products, releasing heat, in burning; or when food is transformed into bone, muscle, and nervous tissue. At other times we seek to prevent or delay these transformations. We would be glad if iron did not rust and wood did not decay; and efforts are always being made to prevent rubber tires from being made brittle by age, and to arrest the slow transformations that finally ruin leather, fabrics, and schoolgirl complexions.

5. Chemistry as a Science

Chemistry as a *science* is concerned (1) with correlating and interpreting facts observed in the practice of chemistry as an art, and (2) with obtaining new facts that seem likely to prove useful in explaining those already known. In brief, *chemical science is a manner of thinking about transformations of materials, which helps us to understand, predict, and control such transformations.* It furnishes directing intelligence in the use of materials. This directing intelligence in the use of materials, and not the discovery of new materials, is the chief contribution of modern chemistry to human welfare and progress. Our own age is chiefly distinguished, not by its possessing more materials than were known in ancient times, but by its ability to make more intelligent use of the materials that it has; and chemical *science* is not so much interested in discovering useful new facts or even in creating new industries as in explaining facts already known.

6. Chemistry the Central Science

Each one of us began to acquire chemical information and thus, in a measure, to study chemistry, the moment he was born. When we first opened our eyes on this interesting universe, we were confronted with the problem of distinguishing different sorts of matter from one another. When we drew our first breath we acquired a personal interest

in respiration, and presently afterward in digestion. These are chemical processes, concerned with transforming matter. We transform dark blood that courses through our veins into bright red arterial blood, with the help of air drawn into our lungs; and we also transform food into muscle, bone, and nervous tissue.

We have been constantly adding to our store of chemical facts since our earliest childhood. When we learned that wood burns, that milk turns sour, that gasoline should not be approached with a lighted match, that rubber is spoiled by oil, that silverware is stained by eggs, that hard water will not form a lather with most soaps, we were learning chemical facts concerning particular types of matter. It is chemical information of an unconscious sort that enables the cook to prepare us an acceptable meal; and chemical skill went into the making of every material object with which we have to deal—our food, clothing, and shelter, and all our comforts, conveniences, and means of recreation.

"Why study chemistry?" "Because we can't help doing it." There are some things, like the law and chemistry, from which no one can escape. Each of us who avoids the penitentiary must live in reasonable conformity with the law; and all the materials that surround our lives, as well as life itself, illustrate chemical principles which would be useful to know.

Chemistry touches all human interests. Jointly with physics, it is really the central science. Its interest in the problems of identifying, separating, or transforming materials makes it of service in all the professions. The rocks and minerals that compose the earth's crust had to be identified and distinguished by chemists before the science of *geology* could make much progress. By chemists, too, some understanding had to be gained of the transformations of materials that accompany the growth of plants and animals, before *biology* could become much more than a mere catalogue of the different species. Before *medicine* and *pharmacy* could emerge from a state in which powdered bone was administered to cure rheumatism and blood drawn to reduce fevers, it was necessary for chemists to make a beginning in determining what sorts of materials and transformations of materials are to be observed in the human body, in health and disease.

In the same way, we may date the beginning of *agriculture* as a science, as distinguished from agriculture as a vocation, from the days of a century ago, when chemists began to learn what sorts of substances growing plants must obtain from the soil and air, and what sorts of changes plants undergo when they decay or are digested by animals.

Engineering, too, owes its most useful materials to the achievements of chemists in identifying, separating, and transforming materials: structural steel for the framework of bridges and buildings, portland cement for roadways and aqueducts, pure copper for the electrical industries, aluminum alloys for automobiles and airplanes, porcelain for spark plugs and electrical insulators. The triumphs of engineering skill rest on a chemical foundation.

7. Chemistry as a Part of a General Education

The applications of chemistry in agriculture, biology, medicine, pharmacy, and the various branches of engineering are a sufficient excuse for its inclusion in the training of students preparing for careers in these special fields. But its importance as a part of a general education has been insufficiently emphasized.

The so-called *cultural studies* are those that summarize the principal intellectual achievements of the human race and permit us to review the most noteworthy things that the mind of man has produced in centuries gone by: masterpieces of literature and art, systems of law and government, ideas of logic and philosophy, triumphs of architecture and engineering, and the great generalizations of science. Among all these, science holds first place in the seeming sureness with which it makes progress, and the promise of permanence in its results. Daily, and more and more, it influences the lives (and thoughts) of all of us—poets and portrait painters no less than physicians and engineers.

Chemistry, in particular, serves as a splendid illustration of what science is, and why some knowledge of its methods and results must be obtained by everyone who hopes to become well educated. Modern chemistry, with its far-reaching generalizations, is a fine example of how far the human mind, aided by precision instruments, can go in exploring the unknown beyond the limits of the unaided human senses. Its industrial achievements, though the wonder of the age, are the least of the reasons why anyone should study it; and many who are first attracted by its reputation for practical utility in the end have come to prize it most for its intellectual beauty.

For those of us who make only a brief study of chemistry, the benefits to be expected are of an indirect nature: *increased capacity for enjoyment, a livelier interest in the world in which we live, a more intelligent attitude toward the great questions of the day*—these are the by-products of a well-balanced education, including chemistry in its proper relation to other studies.

Technical Words

Acquiring an education is a process of developing capacity for thought. So this course in chemistry, as a part of your general education, seeks not so much to impart information as to afford training in the art of thinking. Now thinking about any subject is intimately interwoven with the *use of words*. Thought gains in precision as the words that spring to its aid or are employed in its final expression are more and more sharply defined. Training in the use of words in this manner, with each word restricted to a single precise meaning, is therefore an important part in training in the methods of thought that characterize science. By contrast, a poet may chiefly prize a word for all that it broadly connotes or the emotions that it stirs.

In our study of chemistry we shall encounter a good many words unknown to ordinary, everyday speech. The need for them is made evident by the fact that we shall depart from ordinary, everyday thoughts. Common words tend to be dulled by too much bandying about on the sidewalks of the world; but technical words, like precious stones, preserve their luster and brilliancy.

The first time any important technical word appears in this book it is printed in *italics* and defined or explained by a few words, enclosed within parentheses. If more than a few words are needed to define it, it may be defined at the end of the chapter. The student should make a special effort to master and understand such words, one by one, as they are encountered.

Technical words already defined or explained, in this chapter:

Objects **Materials** **Ceramic** **Chemical union**

Here are some others that need further explanation:

Transform—to convert into something different. To change completely in characteristics.

Art—a craft or occupation, in which skill is based on practical experience as well as on conscious knowledge.

Science—any body of *facts*, marshaled under general principles; also self-consistent *thinking* about such facts, with the purpose of explaining and extending them.

Chemistry—the *art* of identifying, separating, or transforming materials; or the *science* that seeks the general principles underlying such transformations, and their most plausible interpretation or explanation.

Chemical union, or **chemical combination**—an intimate association of two or more materials, in which each so completely alters the properties of the others that a new material results, very different from those that went into it.

The student who has formed the habit of looking up unfamiliar words of any sort, not merely in chemistry but wherever encountered, will eventually acquire the sort of vocabulary by which people are recognized who have really been educated in passing through college or through life. Those who have learned to think about any subject express themselves in words which are so clear and precise that their use clarifies thinking, however unfamiliar such words may be to untrained minds. It is no mere affectation for people with developed talents to use words unknown to others. To some degree the high quality of their minds is due to their habit of making every subject studied contribute to their command of ordinary English—so much are the processes of thought dependent on the words in which thought is expressed!

Exercises

How carefully and efficiently do you read? To test yourself, answer these questions:

1. What are some of the principal inanimate agencies (p. 1) that alter the face of nature?

2. What was the origin of primitive magic and religious ritual?

3. What was the earliest of man's important triumphs over the forces of nature? By what natural events may fire have come to the attention of primitive man?

4. Name several industries, developed among the earliest historical races, that indicate skill in transforming materials.

5. Is porcelain a modern invention? Paper? Steel? Glass?

6. What is meant by the "chemical arts"? Are these older or more recent than the science of chemistry?

7. Do you think science a conscious search for new materials or new inventions, or are these a by-product of the scientific manner of thinking?

8. What is implied by describing science as a "short cut to results that persistence may obtain without the aid of science"?

9. Distinguish between an object and a material.

10. Indicate the three chief tasks of chemistry as an art, with an example of each.

11. Are we always interested in furthering transformations of matter, or do we sometimes wish to restrain or prevent them? Give examples.

12. What are some of the professions in which the science of chemistry plays a part?

13. What are some of the benefits, aside from an acquisition of facts, which an education is supposed to confer?

14. Define chemistry: first, as a practical art; second, as a science.

15. Define: ceramic material, transform, science, chemistry.

16. Mention some transformations of matter, other than those in the second paragraph of § 6, with which everyone probably is familiar.

17. Which of the following do you think are materials and which merely objects: iron, an iron bolt, wood, chunks of wood, milk, sulfur, sulfur crystals, steel rails, a drop of water, air, the atmosphere.

18. The words *art* and *craft* are often used with the same meaning. Can you think of a different meaning, sometimes given to the former?

19. Look up in a dictionary at least half a dozen of the terms listed or defined on the preceding page. Does a dictionary offer difficulty because it fails to define words accurately enough for scientific purposes, or because it offers several different meanings for the same word?

20. Name several things which are ceramic products. (Use the index to this book.)

Chapter 2

ELEMENTS AND COMPOUNDS

8. Physical and Chemical Properties

The *properties* of a material (namely, the characteristics by which it may be identified or distinguished from others) include such items as color, odor, density, tensile strength, electrical conductivity, hardness, melting point, boiling point, ability to refract (bend aside) a ray of light, and capacity for being magnetized. The properties just mentioned are classed as *physical properties*—those that can be specified without considering the capacity of a material for being chemically transformed into a different material.

Chemical properties, by contrast, indicate the capacity (or lack of capacity) of a material for undergoing complete transformations in which all its properties are altered, so that there results a different material, to which we give a different name. When we say that iron is rustable but that platinum is not, or when we say that coal is combustible, that food is digestible, and that ordinary air and water can be converted into nitric acid, we are mentioning chemical properties.

When an engineer purchases materials he may give definite *specifications* with regard to such chemical properties as resistance to corrosion or to destruction by fire, and with regard to such physical properties as density, tensile strength, hardness, and electrical conductivity. (Ex. 1.) [1]

9. Changes in Properties

Changes in the physical properties of a material are often called *physical changes*. Good examples are melting, freezing, evaporation, liquefaction, and formation of crystals. Other physical changes are observed in magnetizing iron or steel, charging a metallic plate with electricity, or heating any material (such as porcelain or platinum)

[1] When an entry of this sort is encountered, turn to the end of the chapter and work the correspondingly numbered exercise or exercises.

that merely shows a temporary change in color when heated, without being permanently altered. The chemical properties of a material, in other words its capacity or lack of capacity for being transformed into other materials, remain essentially unaltered in spite of physical changes, such as those just mentioned.

Chemical changes (often called *chemical transformations*, or *chemical reactions*) are processes in which materials are converted into other materials, with completely different physical and chemical properties. Each of the changing materials is said to *react* with the others, whenever they are *jointly* transformed into new materials. Fuels, for example, react with the oxygen of the air, in being burned.

When one material appears to *dissolve* in another the process is sometimes a mere physical change and sometimes a thoroughgoing chemical transformation.

10. Substances

Among the innumerable materials found in nature there are a relatively small number which (when sufficiently *purified*) are found to possess *definite properties*—in other words, properties that are always the same when observed under constant conditions, regardless of the source or origin of the material. Water, for example, when freed from accidental mineral impurities by distillation, is found to possess a definite set of properties: it freezes at a definite temperature (0°C, under a pressure of 1 atmosphere), boils at a definite temperature (100°C, under a pressure of 1 atmosphere), and at any given temperature has a definite density and a definite index of refraction.

Similarly for many other materials: Common salt, when carefully purified, has a definite set of properties, regardless of its source or origin—regardless, for example, of whether it originally came from the ocean or from a salt mine or was made by burning metallic sodium in an atmosphere of chlorine gas, or by dissolving baking soda in hydrochloric acid. Nitric acid made from the atmosphere is indistinguishable from nitric acid made from sodium nitrate, provided that both samples are pure. (Ex. 2.)

Materials of definite properties are termed *substances*. About a million different substances have been identified.

11. Mixtures and Solutions

When two or more substances are intermingled they may or may not be thereby transformed into new substances, different from those present in the beginning. If no such transformation occurs there is

a mere *mixture* of the original substances. The substances (or, more generally, the materials) that are intermingled in producing any mixture are called the *ingredients* or *components* of the mixture.

Some materials may be recognized as mixtures by the most casual inspection. In graham flour, with the aid of a small lens, one may recognize flakes of bran, grains of starch, and fragments of gluten. In a handful of garden soil the same means will disclose grains of sand of different colors, intermingled with fragments of decaying vegetation. In most building stones there are crystalline particles of different forms and colors. Mixtures in which the intermingled particles are distinguishable with the naked eye or with a simple lens are sometimes called *coarse mixtures.*

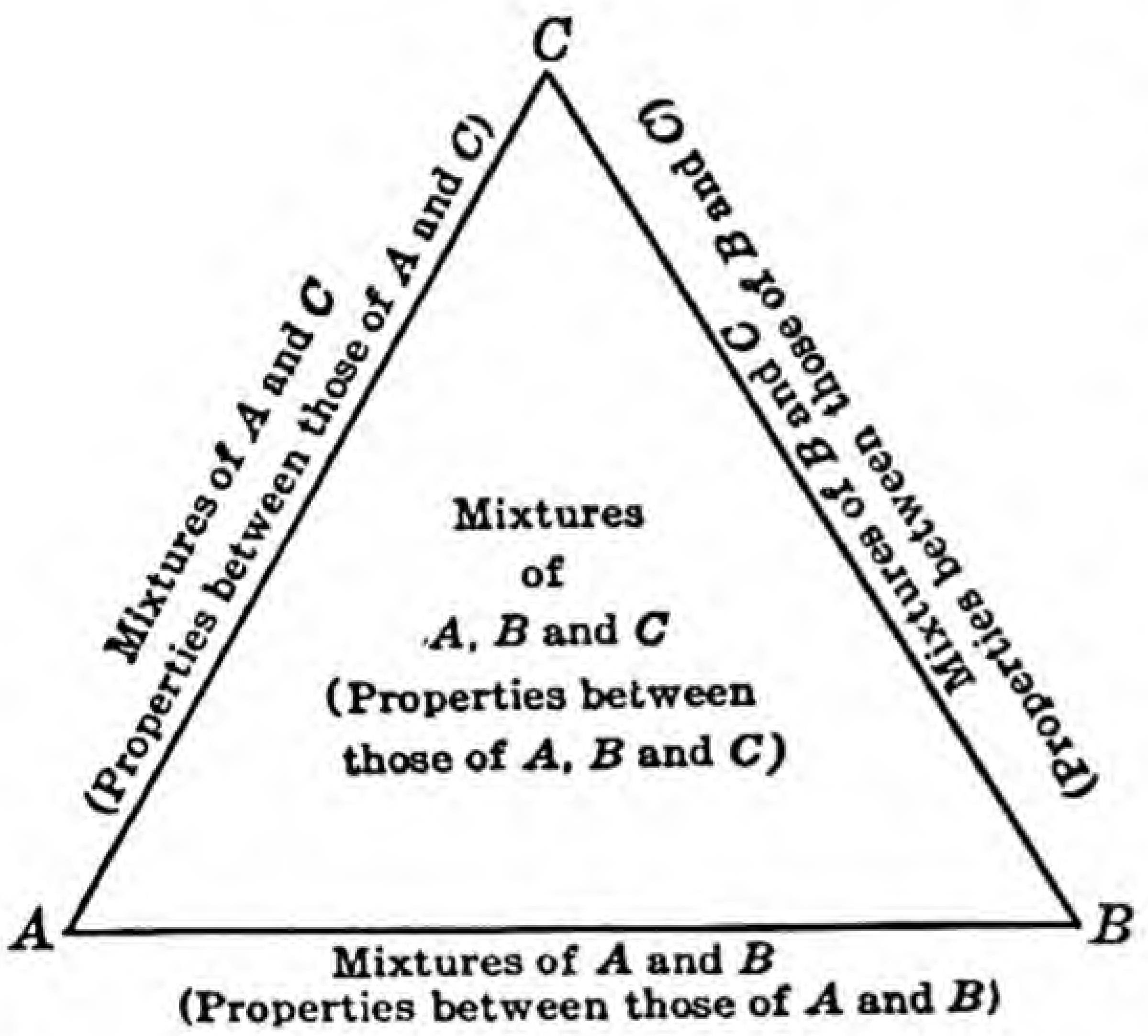


FIG. 4. Diagram to indicate that the properties of a mixture are intermediate between those of the components of the mixture.

Certain other mixtures are recognizable as such only when examined with a powerful microscope. Milk is an example. To the unaided eye it may appear to be quite *homogeneous* (*i.e.*, every portion appears to be exactly like every other portion). Yet the microscope reveals milk to consist of droplets of butterfat dispersed in a watery fluid. Other mixtures (*colloidal dispersions*, § 428) contain particles too fine to be detected by the best microscopes, yet still recognizable with the aid of an ultramicroscope (§ 429); varnishes, skimmed milk, and india ink are good examples.

Finally, we have mixtures that appear to be perfectly homogeneous by all tests, yet betray themselves to be mixtures by the fact that different samples differ from one another in composition and properties. Such apparently homogeneous mixtures are called *solutions.* Sea water is an example. So is glass. So is ordinary air. We see that a solution is not necessarily a liquid.

The properties of a mixture are nearly always intermediate between those of the materials that were intermingled to produce it: Intermingle red and white paint and you get a mixture that is of an intermediate shade, between red and white. Intermingle water with a liquid of

lower *density* (weight per unit volume), such as alcohol, and you get a solution of intermediate density.

If you have a mixture of three different components, A, B, C, the properties of the mixture will be somewhere between those of the three components, as shown in Fig. 4. A mixture of equal weights of the three components would be represented by a point in the center of the triangle. Its color, density, *volatility* (ease of being vaporized) would be an average of these properties for the three individual components. Even its price would be an average price.

12. Combining and Decomposing

In all that has just been said we have assumed that the intermingled materials did not enter into a chemical transformation. Very often they do. Intermingled materials are said to *combine* or to enter into *chemical union* with one another (§ 4) when they pass into an intimate association in which the original materials disappear and a single different material results. Thus the nitrogen and oxygen of the air we breathe may be brought into chemical union with each other and with water—and the result is nitric acid!

The reverse process is to *decompose* a material, namely, to separate (transform) it into two or more other materials, different in their chemical properties from the original material and from each other. No one would ever guess that common salt, with the aid of an electric current, may be decomposed into sodium (a soft, white metal) and chlorine (a greenish gas).

The simpler materials of which a substance is composed or into which it may be decomposed are called its *constituents*.

The student should make a special effort to use the right words in describing what happens in intermingling two or more materials. We may *mix* powdered iron and powdered sulfur to obtain a mere *mixture*, with color and other properties intermediate between those of sulfur and iron, the *ingredients* of the mixture. But when this mixture is heated the sulfur and iron *combine* to form a new material, ferrous sulfide, with completely new properties. Iron and sulfur are the *constituents* of the ferrous sulfide, a definite *substance*. (Ex. 3, 4.)

13. Compound Substances vs. Elementary Substances. Elements

Substances that can be decomposed in chemical transformations are called *compound substances*, *chemical compounds*, or simply *compounds*. In decomposing them into simpler substances, and these

perhaps into simpler ones still, we at length arrive at a few types of matter that resist all attempts to decompose them further by what are termed *chemical methods* (the action of heat or an electric current or interaction with other substances). These practically undecomposable substances are the so-called *elementary substances*. They are classified as metals (iron, copper, etc.) and non-metals (carbon, phosphorus, oxygen, argon, etc.). When one of them occurs in several distinct crystalline forms, these are physically different but chemically identical elementary substances.

The word *element* is a somewhat more general term which includes all the physically distinct forms of a specified elementary substance, whether combined or uncombined with any other element.

14. How We May Determine Whether a Given Substance Is an Element

When we said that the elements are practically undecomposable we meant that none of them has ever been *decomposed* (and none of them has ever been *created*) by chemical methods.

Nevertheless, most of the elements have been decomposed or have been converted into other elements by recently devised *physical methods*, which consist in submitting small samples of material to "bombardment" with almost incredibly swift-moving projectiles, of far less than microscopic size. These experiments (§§ 583–595) show that the elements are not absolutely undecomposable, but are merely very much more difficult to decompose than any compound. Nearly all of the 96 elements now known have thus been created from other elements. Eight of them probably do not exist in nature.

The first well-considered list of elements, in fair agreement with a list accepted today, was drawn up by the French chemist Lavoisier (1789) and revised by his immediate successors. In the years that have since elapsed his list has been gradually corrected and improved.

It was eventually (1869) found possible to classify the elements into groups, so that all those within any one group possessed similar properties; the groups were then placed in successive columns, in the *periodic table* of the elements, § 210. *All the elements in any one column of this table have similar chemical properties.*

A substance which seems to be undecomposable is admitted to the list of elements only if it possesses chemical properties that give it a definite place among other elements in the periodic table.

SUMMARY

Materials

All the different types of matter in the universe

Mixtures		**Substances**	
Materials of indefinite composition and properties. The ingredients or components of a mixture or solution are definite *substances*.		Materials of definite composition and properties	
Coarse Mixtures	**Solutions**	**Compounds**	**Elementary Substances**
(Non-homogeneous mixtures)	(Apparently homogeneous mixtures)	Decomposable substances (over 1,000,000 known); decomposable into simpler compounds, and finally into elementary substances	Practically undecomposable substances

15. Exit Alchemy

To admit that the material universe is composed of a limited number of distinct elements is to admit that *it is possible to convert one material into another* (at least by ordinary "chemical methods") *only when the first material contains all the elements which are necessary for the production of the second.*

The recognition of this fact finally put an end to a hope long cherished by the *alchemists* (predecessors of the chemists of today) that it might be possible to convert other metals into gold. We now know that though such a transformation is conceivable, it would require such elaborate equipment and the expenditure of such quantities of energy as to be worth trying only because of the *information* it might yield concerning the nature of the elements.

With abandonment of the hope of transforming any substance into any other there vanished another dream of alchemy—that a universal medicine, the *alkahest*, might be discovered for the cure of all diseases. So alchemy at length went the way of belief in witchcraft. The thinking part of the human race was becoming less credulous. The day passed in which the multiplication of pearls and the transmutation of other metals into gold had any standing among others than fanatics and cranks. Meanwhile, stories of enchantment and sorcery, in which witches rode abroad on broomsticks and princes became toads, had passed from the beliefs of the multitude, to find a last refuge in fairy books for children. This was more than a chemical awakening.

16. A Cosmic Inventory

Every element, at sufficiently high temperatures, emits light of a definite character or color. When the light from the sun or stars is examined with a spectroscope (§ 234) it is separated into the various sorts of light that compose it, thus revealing what elements emitted it. We may thus determine not merely which elements are present in the distant heavenly body, but also in approximately what proportions. The result shows that the hottest stars (those that glow with bluish white light) are composed of *hydrogen* and *helium*, the lightest known elements. Stars of somewhat lower temperature give evidence of *calcium* and *magnesium;* those of lower temperature still, including our own sun, are relatively rich in *iron*, as well as in calcium, magnesium, and hydrogen. From these data and the approximate relative number of stars of each class it is possible to deduce a rough cosmic inventory, giving the relative abundance of the different elements throughout the stellar universe. All the elements encountered are those familiar on earth. As far as we can tell, chemical transformations in the remotest depths of the universe employ the same elements as transformations here on earth. *No element, still unknown on earth, is known to exist elsewhere.*

17. Meteorites. The Solid Earth

The composition of the earth as a whole may be surmised from that of *meteorites*—a name given to metallic or stony bodies of any sort, arriving at the earth's surface from outer space. Most meteorites are mere specks of dust; larger ones become heated to incandescence, by friction, in passing through the earth's atmosphere, and are then visible as "shooting stars." Occasionally a meteorite weighing many tons has fallen on the earth's surface. Big or little, meteorites have always been eagerly examined as actual samples of material from distant parts of space. Most of them, probably, resemble our own earth in being derived from the sun. So, by analyzing them, and striking a fair average for stony and metallic meteorites, we can get an idea of what would be found in the earth if we could sample it all the way through.

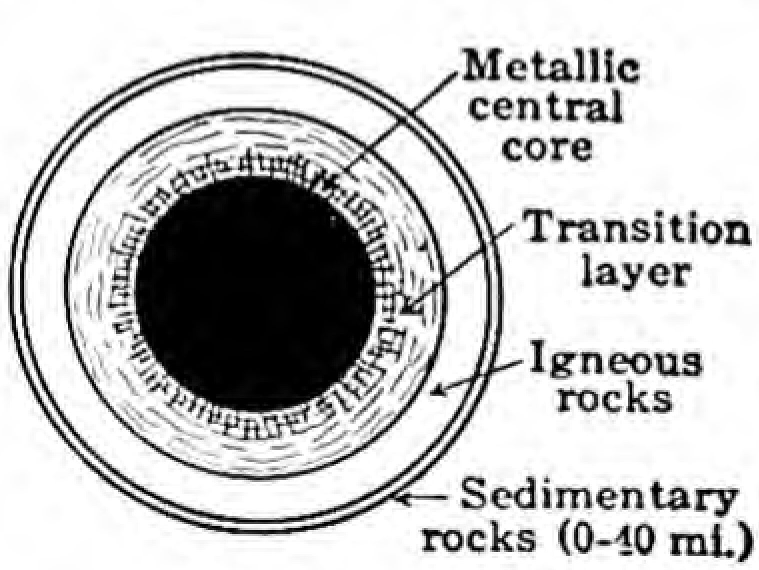


Fig. 5.

We are thus led to believe that *iron* is the most abundant terrestrial element, with *nickel, calcium*, and *magnesium* less abundant, but still important. Indeed, the earth as a whole has a density and propagates

earthquake shocks in such manner as to suggest the assumption that it is simply a ball of solid iron, or iron-nickel alloy, about four thousand miles in diameter, overlaid with a layer (about a thousand miles thick) in which these metals gradually give place to stone, then with another layer (also about a thousand miles thick) consisting chiefly of igneous rocks, for the most part *solid* (Fig. 5).

18. Elements of the Earth's Crust

If the earth's elements were once everywhere distributed in the proportion shown by our cosmic inventory, it is certain that they are not so now. The stony outer layers of the earth have been depleted of the heavier elements and enriched in the lighter ones. Iron has yielded precedence to oxygen and silicon. If we limit our examination to the part of the earth's exterior that is directly accessible, namely, to the atmosphere, the ocean, and rocks *that can be reached and sampled*, we find that *oxygen* makes up about one half of this layer, often called the "earth's crust." *Silicon* makes up about one fourth; then in order follow six metals: *aluminum*, *iron*, *calcium*, *sodium*, *potassium*, and *magnesium*. With these eight elements we dispose of about 98 per cent of the earth's crust. All the remaining elements, at least 82 in number, constitute only about 2 per cent.

We are astonished to note that iron is the only heavy metal that is present in the earth's crust in any large proportion. Other useful and familiar heavy metals, such as lead, zinc, and copper, are probably each present in the earth's crust in quantities of less than 0.01 per cent; whereas tin, gold, silver, platinum, and some other elements of importance to industry are much less plentiful still.

Most of the less familiar elements are exceedingly rare: indium and rhenium, for example, are probably present in the earth's crust in a proportion not to exceed *one part in a million million*. To detect any one of them in a sample of rocky material selected at random would be like seeking a particular individual among the entire population of the earth. Rhenium and some other rare metals are, indeed, never found in any mineral in greater abundance than 0.001 per cent. A ton of the richest ore found anywhere on earth, if completely extracted, would yield at most only about one-third ounce of the element sought. In traces, nevertheless, the rarer elements are very widely distributed. If we possessed analytical methods of sufficient delicacy we might find traces of all of them in every handful of garden soil or in a sample of sea-water. (Ex. 5.)

19. Wherein Chemistry Meets Geology

During long ages the geologic agencies of running water, scouring ice sheets, and atmospheric oxygen have crumbled and worn away the solid rocks, leaching from them the more soluble minerals, and leaving behind the less soluble ones. Pressure and volcanic heat have induced chemical transformations in which certain elements have been involved and others passed by. By this continuous sorting and resorting of the elements, during the course of ages, workable deposits of useful minerals and ores have been brought into existence: copper, zinc, lead, tin, and even rhenium. Bacteria at length arrived to play their part in the interchange of the elements, engaging during uncounted centuries in activities that here produced a great deposit of iron ore and there a million tons of sulfur. Higher plants and animals, during recent millennia, have done their part in the never-ending sorting and resorting.

Man seems chiefly destined to dissipate the stores of raw materials that nature so patiently assembled long before the race of man appeared on earth. This is not a serious prospect if the raw materials are compound substances that happen to be composed of common elements. When petroleum is gone a substitute may be made from coal; and real camphor could be made from turpentine if the camphor tree were to become extinct. This is true because petroleum and camphor are compound substances containing elements (carbon, hydrogen, and oxygen) that are available to us in inexhaustible quantities.

But, previous to the recent synthesis of four new elements, quite unknown in nature (§ 593), no element had ever been produced in usable quantities from any other element. This feat cost two billion dollars. When the supplies of certain rare elements (such as cerium, platinum, and even tin) are exhausted, mankind will probably have to do without the compounds that may be produced from them, unless methods can be developed to recover them from the traces that exist in the ocean water, or unless the transformation of one element into another, by methods now being developed, finally becomes much cheaper than at present.

Technical Words

Study the following definitions, and be prepared to restate and illustrate them

Properties, p. 10.
Physical properties and **chemical properties**, p. 10.
Physical change and **chemical change**, pp. 10, 11.
Reaction or **chemical transformation**, p. 11.
Mixture, p. 12. **Solution**, p. 12.
Ingredient or **component**, p. 12. **Constituent**, p. 13.

Disperse (verb)—to subdivide a material and scatter its particles through another.

Dissolve—to disperse one material in another, with or without chemical alteration, to produce an apparently homogeneous mixture, *i.e.*, a solution.

Combine or enter into **chemical union,** p. 13. **Decompose,** p. 13.

Impurity—an accidental ingredient, intermingled in relatively small amount with some other material and modifying its properties. Example: iron oxide, present in traces, as an impurity in sand, may give a distinct greenish color to glass made from the sand.

Substance, p. 11. **Element,** p. 13. **Compound,** p. 13.

Composition or **chemical composition**—the *identity* and *relative proportions* of the ingredients of a mixture or the constituents of a compound. The composition of ordinary water, for example, is 11.19 per cent hydrogen and 88.81 per cent oxygen.

Density—the mass or weight of unit volume of a material; usually, the weight in grams of 1 cc.

Specific gravity—relative heaviness of a material, in comparison with some other material (usually water). A specific gravity of 5, for example, would mean that the given material weighs 5 times as much as the same volume of water.

Periodic table—a table of the elements (§ 215) arranged in rows and columns, the different columns representing different groups of chemically similar elements. The order of the elements within the table is determined by the nature of the X-rays they may be made to emit (§ 216).

Spectroscope—an instrument with the aid of which elements and occasionally compounds may be identified, by a study of (1) the light that they emit at high temperatures, or (2) the light that they absorb.

Incandescent—so hot that visible light is emitted.

Cosmic—relating to the universe in general, including our earth as a part of it.

Mineral—any element or compound occurring in nature and possessing reasonably definite composition and properties, even though somewhat impure. Most minerals are solids; but in the broadest sense even water is a mineral. *Coal* is not classed as a mineral, because it is a complicated mixture, with widely varying characteristics. **Rocks** are sometimes definite minerals and sometimes mixtures of minerals.

Ore—a mineral from which one or more metals is obtained as a commercial enterprise.

Summary

When the definitions in the preceding list have been made thoroughly familiar, go over the chapter again in an effort to understand it better. You should then be able to state:

§ 8. What is meant by properties. Distinction between physical and chemical properties.

§ 9. Distinction between physical and chemical changes.

§ 10. Some very definite properties possessed by carefully purified water.

The name given to materials which, when purified, are found to possess a definite set of properties.

§ 11. Some examples of mixtures. Name given to the materials that are intermingled to produce a mixture.

What is meant by saying that a material is homogeneous. Some examples of homogeneous materials. The general name given to homogeneous mixtures.

How a triangular diagram may be made to represent the properties of a 3-component mixture.

§ 12. What we mean by decomposing a material.

§ 13. A general name given to pure substances that are decomposable. A general name given to substances that resist all ordinary attempts to decompose them.

In what respects the different forms of an elementary substance, such as sulfur, are really different, and in what respects identical.

§ 14. Whether elements are really undecomposable, or only practically so.

What can be said about all the elements within one group or vertical column in the periodic table.

How we may determine whether a given substance is really entitled to be recognized as an element. How many elements are recognized today.

§ 15. The two chief hopes of alchemy, discredited by modern chemistry.

§ 16. What instrument is used in determining the chemical composition of the sun and stars. What elements have been observed to be plentiful in stars of different temperatures and in our own sun. Whether elements still unknown on earth are believed to exist in distant stars.

§ 17. Name given to stony or metallic particles arriving at the earth's surface from outer space. Why their chemical composition is of interest.

What is believed to be the inner structure of the earth. On what evidence.

§ 18. What actual part of the earth is included in the term "earth's crust." The percentages of oxygen and silicon in this surface material. What six elements are next in quantity. Whether the common heavy metals, such as zinc, lead, and copper, are relatively abundant or relatively scarce in the earth's crust.

§ 19. Four or five inanimate geologic agencies which have sorted and worked over the elements of the earth's crust during ages past.

Exercises

1 What physical properties are probably most important, and what chemical property needs also to be considered in each of the following: coal, rubber, gasoline, iridium tip for a fountain pen, steel for a woven wire fence, dough for making biscuits?

2. From the examples in § 12, do you think that it usually is or is not possible to predict the properties of a substance from those of the elements contained in it?

3. By intermingling two or more metals (ordinarily by melting them together) alloys are frequently made that are superior (§ 499) in hardness, resistance to corrosion, and other useful properties to the individual metals contained in them. Do you conclude that such alloys are solutions or compounds? Why?

4. Would you speak of the ingredients or constituents of a lemon pie? Why?

5. Attempts have been made to extract aluminum from clay, but clay is so very impure that they have not been commercially successful in competition with methods using other raw materials. Which of the following terms therefore may be applied to clay: ceramic raw material, mineral, ore, substance, compound?

Chapter 3

ATOMS AND MOLECULES

"For the things that are seen are temporal, but the things unseen are eternal."

20. Atoms

From any compound or from any mixture of compounds you may (if you know how) recover, undiminished in weight, all the elements that originally went into it. To express it otherwise: The ninety-odd elements may assume disguises by being altered or transformed individually, or by being combined with one another; nevertheless, their *identity as elements* is conserved. Select what elements you will; combine and recombine them through the ages. In the end they will still be there, in their original proportions.

The eventual recovery of an original set of elements, after these have apparently been destroyed in forming compounds, suggests that matter is composed of indestructible *particles*, which preserve their identity through all the turmoil of chemical change, remain undiminished and unworn through all the ages, and are at length recoverable in their original kinds and numbers. These apparently eternal, indestructible, and indivisible particles, far too small to be perceived by our best microscopes, and serving as building stones of the universe, are called *atoms* (*Greek:* indivisible).

The existence of atoms was assumed by certain philosophers among the ancient Greeks (about 600 B.C.) for reasons that have been forgotten. The fact (1) that metals expand when heated, and (2) that salt will dissolve in water perhaps originally suggested that metals consist of separate particles which are driven apart by heat, and that water consists of separate particles with spaces between them large enough to accommodate the particles of salt. To us, the existence of such elementary *particles*, more eternal than the hills, seems sufficiently attested by the apparently eternal nature of the *elements*.

21. The Law of Conservation of the Elements

Chemistry, like the other sciences, is concerned with discovering, classifying, and reviewing a multitude of apparently disconnected facts, in an effort to disclose important laws. (A **law**, in science, is a *general statement*, summarizing a multitude of separate observations, and expressing what is thought to be *the invariable consequence of a given set of conditions.*)

Most fundamental of the laws of chemistry is one that chemists and chemical textbooks usually take for granted, without giving it the special prominence that it deserves. It may be called the Law of Conservation of the Elements: *No chemical reaction ever converts one element into another.* To convert one element into another, we need something else than "ordinary chemical methods." We must submit samples of the element to bombardment by swift-moving material particles, of less than microscopic size.

22. The Law of Conservation of Mass or Matter

The Roman poet Lucretius, 2000 years ago (96–55 B.C.), expressed the time-defying nature of the atoms by saying that atoms are of "pure solidity." We may readily infer that they remain *undiminished in weight*, in combining and recombining to form complex particles. Thus whenever a material is chemically altered to produce one or more new materials there should be no detectible change in weight.

This principle was first clearly stated by Lavoisier (1776). It was well established by his own work and has been confirmed by that of all later workers: *However thorough the change of properties may be, in transforming one set of materials into another, one property, the total weight, is not perceptibly altered.* Apparent loss or gain of weight, in any chemical transformation, is always found to be due to failure to take note of all that happens—failure, for example, to observe that a part of the air combines with substances that burn in air, or that most substances when burned yield gaseous products, readily overlooked.

Otherwise expressed: *In any chemical reaction the sum of the weights of the original materials* (often designated as the **reactants**) *is not perceptibly different from the sum of the weights of the materials produced* (often designated as the **reaction products** or **resultants**). So when a candle burns, combining with oxygen of the air, and producing carbon dioxide gas and water vapor:

$$\text{Weight of candle} + \text{Weight of oxygen combining with it} = \text{Weight of carbon dioxide} + \text{Weight of water vapor}$$

The heat and light set free when the candle burns have no detectible weight and so may be disregarded. (Ex. 1.)

Since weight is one measure of *mass* (p. 28), which in a certain sense indicates the "quantity of matter" in a body, the inference is that *chemical reactions merely transform matter, never create or destroy it.* This is the *Law of Conservation of Mass or Matter.*

23. The Law of Definite Proportions

The successors of Lavoisier, during two generations, established another important fact: *Every substance, in being burned, combines with some definite relative weight of oxygen.* (By *relative weights* we mean weights stated in comparison with each other.) For example, when carbon burns in a plentiful supply of oxygen, the weight of oxygen combining is always $2\frac{2}{3}$ times the weight of the carbon; that is, the relative weights of oxygen and carbon are as $2\frac{2}{3}$ is to 1. This may also be expressed as the ratio of 8 to 3, or as 16 to 6, and so forth. If we burn 1 gram of carbon we shall need $2\frac{2}{3}$ grams of oxygen; if we burn 3 grams of carbon we shall need 8 grams of oxygen; and 1 pound of carbon will need $2\frac{2}{3}$ pounds of oxygen. These are *experimental facts*, not based on any theory. (Ex. 2.)

When hydrogen is burned in oxygen, the product is ordinary water. The weight of the oxygen combining is 7.9365 times the weight of the hydrogen; that is, the relative weights of the combining elements are as 7.9365 to 1, whether we burn much hydrogen or little. This is another experimental fact. (Ex. 3.)

With other reactions, whatever substances are involved, the same experience holds: *Any given chemical change transforms invariable relative weights of the reactants and produces invariable relative weights of the reaction products. This is the Law of Definite Proportions.*

In consequence, a chemist may make tests on a small scale to determine what quantities will be needed when operating on a large scale. He may carry out an experiment involving quantities of material that may be heaped upon a dime, observing relative weights which will enable him to predict surely what weights will be needed in dealing with these reactants in carload lots. It is as if nature always worked with *standardized recipes.*

24. The Law of Constant Composition

The Law of Definite Proportions has an interesting consequence. It implies that, when *elements* combine to form any given compound, they will do so in invariable proportions by weight. Experiment shows

that 1 part by weight of carbon is needed for every $2\frac{2}{3}$ parts by weight of oxygen, to form carbon dioxide; and 1 part by weight of hydrogen for every 7.9365 parts of oxygen, to form water. In brief, *any given pure compound, no matter how prepared, contains definite elements, in invariable proportions by weight;* in other words, *every compound has a definite chemical composition.* This special case of the Law of Definite Proportions is called the *Law of Constant Composition.* Compounds and elements, then—in brief all materials which are classed as *substances*—possess not only *definite properties*, as already emphasized (§ 10), but also *definite composition.* (Ex. 4, 5.)

The Law of Conservation of Mass and the Law of Definite Proportions are a more serious restraint on chemical transformations than the alchemists ever dreamed. The practice of magic or witchcraft in the twentieth century is seriously hampered. In transforming a prince into a toad, the toad must weigh as much as the prince. Furthermore, the complex substances that compose a prince contain definite elements; and the same elements, in the same proportions by weight, must at length be found in the toad. Faced with such requirements, witchcraft confesses itself baffled, in spite of all toil and trouble.

25. Dalton

The Law of Conservation of Mass and the Law of Definite Proportions were definitely stated and well on their way to being established without any clear picture being drawn of the part that atoms play in chemical transformations. Then, in 1808, the ancient concept of atoms, inherited from the Greek philosophers and largely forgotten, was given increased precision by John Dalton, an English schoolmaster.

Dalton seems to have been impressed by the fact, then recently observed, that when *gases* are chemically transformed their *volumes* are simply related (details, § 85). This suggests that chemical transformations are accomplished by combining and recombining the atoms themselves in some simple way. Dalton's contributions to what we now call the *Atomic Theory* included three ideas:

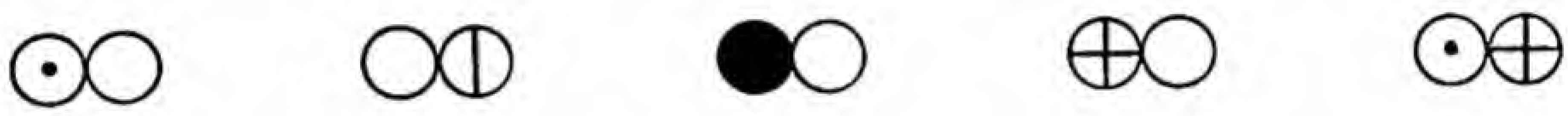
1. *There are as many different kinds of atoms as there are different elements.* Dalton thought of the atoms of any given element as being exactly alike, in particular as possessing exactly the same weight. We now know that different atoms of the same element often differ in weight, though they usually do possess a definite *average weight.* Except for *weight* or *mass*, all the atoms of any given element are *chemically identical.* By this we mean that they all react in the same manner with the atoms of other elements.

2. *Atoms remain undivided in chemical transformations.* Otherwise expressed, chemical transformations are accomplished by combining *whole numbers of atoms*, thus forming *compound atoms*, now called **molecules** (*Latin:* a small mass); or by bringing the atoms that compose any given set of molecules into new groupings and combinations.

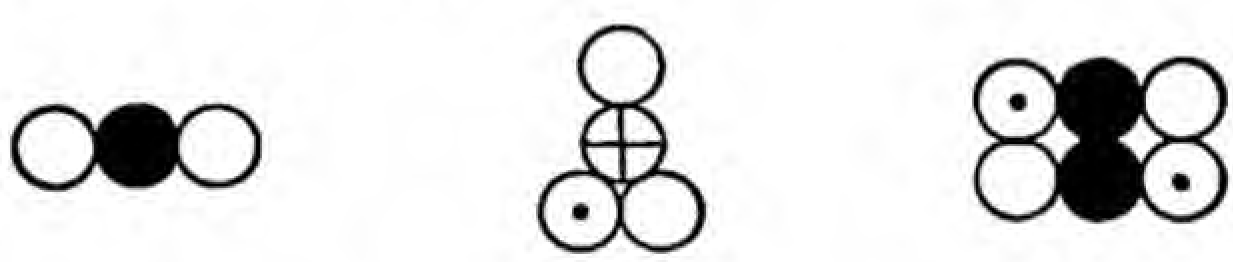
3. *The molecules of any given compound contain a definite number of atoms of each of the elements composing the compound.* Thus a molecule of water vapor, as subsequently shown, contains two atoms of hydrogen and one atom of oxygen.

Dalton represented atoms of the different elements by circles:

Molecules of different compounds then appeared as combinations of one atom with another,



or as more complicated groupings still:



26. The Laws Explained

Dalton's views explain the three laws of chemical change:

1. *No reaction ever converts one element into another* (Law of Conservation of the Elements) because no reaction ever converts one kind of atom into another.

2. *Total weight remains unchanged* (Law of Conservation of Matter) because the atoms entering into a reaction merely become attached to one another, and retain their original weights.

3. *Definite relative weights of the reactants are demanded and definite relative weights of the resultants are produced* (Law of Definite Proportions), because every reaction is accomplished by constructing or breaking down molecules, each containing *definite numbers of particular sorts of atoms*, of *definite average weights.* (Ex. 6, 7.)

27. Atoms vs. Molecules

To make sure that we are clear about the distinction between atoms and molecules, let us recall:

1. There are as many chemically different kinds of *atoms* as there are different elements—in other words, something over ninety; but there are as many different kinds of *molecules* as there are different types of matter, by which we mean *all possible variants of all known substances*—in other words, perhaps a million.

2. A molecule of an *element* may consist of a single atom or of several atoms, *chemically identical.* A molecule of a *compound* contains one or more atoms of each of its constituent elements. The largest and most complicated molecules contain thousands of atoms.

3. *Molecules are the particles that give character to the different individual types of matter.* The diamond is hard, sugar is sweet, rubber is elastic, and gasoline will vaporize and burn because their molecules in some way make them so.

4. *A molecule is the smallest particle that would be recognized as belonging to a given type of matter.* That is what is meant by defining a molecule as an *ultimate particle* of a particular kind of matter. A molecule possesses the *chemical properties* of the given kind of matter; namely, it will enter into the same reactions, to form the same products; but certain *physical properties* (melting point or cleavage, for example) are determined by *groups of molecules.*

5. *To decompose molecules is to obtain molecules of simpler substances or, in the end, atoms of the different elements that are present.*

28. Five Types of Chemical Change

Dalton's ideas about atoms and molecules suggest that chemical changes are of five fundamental types:

1. **Direct union**—a chemical change in which two or more atoms or molecules become attached to one another, to produce a more complex molecule. Representing atoms by circles:

Ⓐ, combining with Ⓑ, yields ⒶⒷ

2. **Decomposition**—a chemical change in which a molecule is separated into two or more simpler molecules (or, ultimately, into the individual atoms of which the original molecule was composed). For example:

ⒶⒷ, decomposed, yields Ⓐ and Ⓑ

3. **Internal rearrangement**—a chemical change in which the atoms that compose the molecule are brought into new arrangements in space

with respect to one another—as if one were to enter a room and shift all the furniture into new positions. For example:

Ⓐ
ⒶⒷⒸ yields ⒶⒸⒷ or ⒷⒸ

4. **Transfer or displacement**—a chemical change in which one or more atoms are transferred from one molecule to another:

Ⓐ reacting with ⒷⒸ yields ⒶⒷ and Ⓒ

This may be viewed as a *transfer* of B from BC to A, or as the *displacement* of C by A, when A combines with B.

5. **Exchange**—a chemical change in which certain atoms in one molecule are exchanged for those in another: ⒶⒷ reacting with ⒸⒹ yields ⒶⒹ and ⒸⒷ. Exchange is sometimes called *double decomposition.* (Ex. 8.)

29. Chemistry as a Mode of Thought

Dalton's work was the first step in a development that justifies us in regarding the chemistry of today as a mode of thought, in which visible transformations of material things are so far as possible *explained*, by assuming certain things about invisible particles. At the same time, such transformations are made capable of *prediction* and *control*. Thus the chemical mode of thought leads to many practical applications.

Though Dalton accounted for the laws of weight relations, and though his successors revealed how many atoms of each kind are contained in any given kind of molecule, plenty of questions still remain. Do atoms really exist? Are they really unalterable and eternal? What holds them together in chemical union? What actually happens in such physical transformations as melting, freezing, evaporation, and the formation of crystals? What happens in a multitude of individual chemical transformations, and how may each be brought about or controlled? What is the nature of electricity, and what happens when chemical transformations are induced by an electric current?

To answer these and many other questions we must penetrate a realm where our ordinary human senses yield only indirect evidence, and where only the inner eye of the mind may direct our steps, with the aid of such precision instruments as intelligence can create. Our ultimate aim is to answer questions of whatever kind with regard to material transformations in terms of atoms and molecules and perhaps other unseen particles. In so far as one learns to do this, interpreting

visible events in terms of invisible particles, one will have acquired the special manner of thinking that is the essence of modern chemistry.

Technical Words

Particle—a small fragment of matter, visible or invisible (such as a particle of dust).

Atoms—the nearly indestructible particles of which matter is composed. There are as many chemically different kinds of atoms as there are different elements.

Atomic-molecular theory—the view that all matter is composed of molecules, the component parts of which are atoms; and that these atoms accomplish chemical transformations by combining or separating or by being rearranged or transferred with respect to one another, thus forming new or different types of molecules. The science of chemistry attempts to learn the details of what happens in each transformation.

Mass—a characteristic that is sometimes said to measure the quantity of matter in a body, since the addition of more particles to a body makes a proportionate increase in its mass. The mass of a body is measured (1) by its *weight*, (2) by the *force* that is needed to alter the rate of motion of the body by a specified amount within a specified time. A body having a considerable mass (a loaded truck, for example) not only weighs a great deal but requires a great force to alter its rate of motion by any specified amount, within any specified time.

Do not confuse mass with mere **bulk** (space occupied).

Conservation—failure to be altered in amount, in spite of alteration in character.

Scientific law, p. 22.
Decomposition, p. 26.
Direct union, p. 26.
Transfer or displacement, p. 26.
Relative weights, p. 23.
Exchange reaction, p. 27.
Reactants, p. 22.
Resultants or reaction products, p. 22.
Internal rearrangement, p. 26.
Ultimate particle, p. 26.

Summary

§ 20. What fact about elements is considered the most convincing evidence that matter is composed of indestructible particles?

Indicate two facts which may have suggested to Greek philosophers that solids and liquids, though apparently continuous, are really composed of separate particles.

§ 21. State the most fundamental or important law governing chemical transformations.

§ 22. What property of reacting substances remains unchanged in spite of chemical transformations?

State the Law of Conservation of Matter, employing the terms reactant and resultant.

Explain how this law would be illustrated in a reaction in which limestone is decomposed by heat, forming quicklime and carbon dioxide gas.

§ 23. State the Law of Definite Proportions, and illustrate for carbon burning in a plentiful supply of oxygen.

This law is sometimes said to be an example of predicting with test-tube quantities what will happen with carload quantities. Explain.

§ 24. Show how the Law of Constant Composition follows from the Law of Definite Proportions.

§ 25. State the three ideas contributed by Dalton to the atomic theory of today. What was Dalton's nationality, and in what year was his work published?

§ 26. Be able to explain in your own words how the views of Dalton explain (1) conservation of the elements, (2) unchanged total weight, and (3) definite relative weights of the reactants and resultants, in a chemical transformation.

§ 27. How many chemically different kinds of atoms are there? How many different kinds of molecules? Are the properties of a material most directly determined by its molecules, or by the atoms contained in them?

§ 28. Explain what happens in each of the five fundamental types of chemical change.

§ 29. What is said concerning the purpose of chemistry, regarded as a mode of thought?

Exercises

The exercises in this and succeeding chapters are to be worked as references to them are encountered, in studying the text. For most of them we shall give *code answers*, which correctly indicate three significant figures, but fail to locate the *decimal point* or to *name* the *unit* in which the result is expressed. You are to give both.

1. Forty grams of a substance A react with 50 grams of B, to produce 10 grams of C, an unstated weight of D, and *nothing else*. What must D weigh if the Law of Conservation of Matter holds accurately? (For a definition of a gram, see Appendix A.) 800

2. If 1 part by weight of carbon combines with $2\frac{2}{3}$ parts by weight of oxygen, forming carbon dioxide, what total weight of carbon dioxide will be formed? Then what percentage of carbon dioxide is oxygen? 367, 727

3. From the proportions by weight in which hydrogen and oxygen combine, in forming water (§ 23), determine what weight of water can be formed from 5 grams of hydrogen. 450

4. If 5 grams of an element A combine with 15 grams of B, what weight of each element (in pounds) will 1 lb of the compound contain? 250, 750

5. Zinc combines with very nearly half of its own weight of sulfur in forming zinc sulfide. Then if 5 grams of each element are taken, what weight of the sulfide is formed, and what weight of which element remains uncombined? 750, 250

6. If we assume that a molecule of ammonia contains one atom of nitrogen, weighing 14 units, combined with three atoms of hydrogen, each weighing 1 unit, what will be the total weight of an ammonia molecule? Then if we had enough ammonia molecules to make 17 lb of ammonia, how many pounds of each element would be present? 170, 140, 300

7. If each molecule of a certain compound contains one atom of carbon, weighing 12 units, combined with two atoms of oxygen, each weighing 16 units, what fraction and what percentage by weight of this compound is carbon? $\frac{3}{11}$, 272

8. Each of the capital letters below represents one *atom* of some element. An arrow means "yields" or "produces."

What type of reaction (§ 28) or what combination of types is represented by each of the following reactions:

$$\begin{matrix}N\\N\end{matrix}O \rightarrow \begin{matrix}N\\N\end{matrix} + O$$

$$CO + O \rightarrow OCO$$

$$HOOH \rightarrow HOH + O$$

$$\begin{array}{l} C + HH \\ O \end{array} \rightarrow \begin{array}{c} HCH \\ O \end{array}$$

$$CO + HH + HH \rightarrow \begin{array}{c} H \\ HCOH \\ H \end{array}$$

$$HSH + \begin{array}{c} I \\ I \end{array} \rightarrow HI + HI + S$$

9. In the following paragraph, underline the proper word to choose from each group enclosed in parentheses.

Every (object, material, substance) has a definite (bulk, size, mass), which may be determined by weighing it. It may contain one or more different (compounds, materials, substances), which may or may not themselves be mixtures. The (ingredients, elements, constituents) of any mixture may or may not be decomposable. If they are not they are entitled to be called (elementary substances, elements).

10. Supply a good word (from among several sometimes possible) for each blank in the following paragraph:

There are five distinct ________ of ________ change. Each is accomplished by rearranging and recombining ________. In that way the ________ of the original ________ are converted into ________ of the final ________. When a material ________ has been sufficiently ________, all samples of it are found to have identical ________.

11. Supply a good word for each of the following blanks:

The properties of every ________ are determined by its ________, and only indirectly by the ________ within the ________. So if a sample of any material is divided into smaller samples, and these into smaller ones still, we would finally obtain a single ________, which is the smallest possible sample with all the ________ properties of the original ________.

12. What differences do you perceive between the meanings of words in each of the following groups:

alter, reshape, transform
mix, combine, react
mineral, ore, rock

13. Indicate differences:

ingredient, constituent
mixture, compound, substance, solution
element, elementary substance

14. Indicate differences:

density, specific gravity
bulk, size, mass
atom, molecule, particle

Chapter 4

WEIGHTS AND FORMULAS

> This chapter may be postponed until a convenient later date if the laboratory schedule demands prompt consideration of oxygen, hydrogen, and the laws of gases. The chemical formulas of the next few chapters will then need to be accepted on faith, in advance of any indication of how they are derived.

The work of Dalton explained chemical changes as being accomplished by combining and recombining *whole numbers of atoms*. But all the details still needed to be worked out. Chemists still needed to discover, for every known substance, *what kinds of atoms* are present in a molecule of the substance, and *how many atoms of each kind*. That information, when finally obtained, gave us the chemical formulas by which all chemical substances are now represented.

Fifty years passed before that problem was completely solved. Then an Italian chemist, Cannizzaro (*Kah-need-zah'ro*), first showed how to obtain the *relative weights* of atoms and molecules (in other words, their weights *in comparison with one another*).

30. Molecular and Atomic Weights

Our standard of weights, in the comparisons we are about to make, is the average weight of an atom of oxygen, taken as 16 units. (We specify the *average* weight of an atom of oxygen, since an occasional atom of oxygen weighs a little more than the others.) We shall presently show (§ 38) that *a molecule of oxygen contains two atoms*. So, instead of saying that an *atom* of oxygen represents 16 weight units we might just as well have said that a *molecule* of oxygen represents 32 weight units.

Oxygen has been made the standard of comparison because it combines with most other elements, and in so doing yields data that we

shall need to use; and an *atom* of oxygen is chosen to be 16 units (or a *molecule* of oxygen to be 32 units) because the lightest known material particle, an atom of hydrogen, then has a weight of very nearly 1 unit.

Relative weights of *molecules*, in comparison with a sixteenth part of the average weight of an *atom* of oxygen, are called **molecular weights.** Relative weights of atoms, likewise in comparison with a sixteenth part of the average weight of an *atom* of oxygen, are called **atomic weights.** Observe that the basis of comparison, in both cases, is the *atom* of oxygen, taken as 16 units (or a *molecule* of oxygen, taken as 32 units). (Ex. 1–3.)

31. Avogadro's Principle

The key to molecular weights is a principle first recognized by another Italian chemist, Avogadro, in 1811: *Equal volumes of all gases and vapors, when observed under the same conditions, contain very nearly the same number of molecules.* For example, a liter of hydrogen gas contains very nearly the same number of molecules as a liter of oxygen or carbon dioxide or any other gas or vapor, *provided that all are observed at the same temperature and under the same pressure.* Reasons for believing that this principle is true will appear in a later chapter (§ 110). Observe that gas volumes are usually measured in *liters.* A liter is a little more than a quart.

Now a liter of oxygen is actually very nearly 16 times as heavy as a liter of hydrogen, observed under the same conditions. If we have nearly the same number of molecules in each liter of gas, then *each individual molecule* of oxygen must be nearly 16 times as heavy as a molecule of hydrogen.

Similarly, any given volume of sulfur dioxide is very nearly $3\frac{3}{4}$ times as heavy as the same volume of ammonia. If we have nearly the same number of molecules in each gas, then each individual molecule of sulfur dioxide must be very nearly $3\frac{3}{4}$ times as heavy as a molecule of ammonia. (Ex. 4, 5.)

32. Approximate Molecular Weights

To determine the molecular weight of a gas or vapor, at least roughly, we need only fill a large, thin-walled flask with the material, weigh it, and compare the weight with that of the same volume of oxygen, under identical conditions. A gas with five times the density of oxygen (*i.e.*, one that weighs five times as much as the same volume of oxygen) must have molecules that are individually five times as heavy as oxygen mole-

cules. If we assign to an oxygen molecule a weight of 32 units, for reasons already given (§ 30), a molecule of the other gas or vapor must weigh $5 \times 32 = 160$ units. Similarly for other substances that are gases or vapors, or for liquids and solids that are readily vaporized. (Ex. 6–8.)

Molecular weights thus found are only *approximate*, since equal volumes of gases and vapors, under identical conditions, contain only roughly the same number of molecules. A few results are given in the accompanying table.

Approximate Molecular Weights of a Few Common Gases and Vapors

(Determined by weighing them, under atmospheric pressure, and comparing their weights with that of the same volume of oxygen, under the same conditions.)

Ammonia	17	Carbon tetrachloride vapor	154	Nitrogen	28
Carbon dioxide	44	Helium	4	**Oxygen**	**32**
Chlorine	72	Hydrogen	2	Sulfur dioxide	64
Chloroform vapor	121.6	Methyl chloride vapor	51.7	Water vapor	18

For other substances, not gases or vapors, molecular weights must be determined by other methods, to be discussed hereafter. Most important are determinations of the *freezing points* or *boiling points* of solutions (§ 297). With their help it is possible to determine the approximate molecular weight *of any substance that dissolves, without reacting, in water or any other solvent.*

33. Approximate Atomic Weights

The relative weights of the *molecules* of a considerable number of substances having been established, the relative weights of individual *atoms* composing these molecules can readily be determined. These are *atomic weights.*

To determine the atomic weight of an element, four steps are necessary:

1. Determine the molecular weight of each of a large number of compounds, *all containing the given element.*

2. Determine (by careful experiments) what percentage of the given element is contained in each of the chosen compounds.

3. We may then calculate what weight of the given element is present *in one molecular weight* of each compound. (Be sure to note the words in italics!)

4. The *least* weight thus found is assumed to be the *least possible* weight of that element in the molecular weight of any of its compounds, namely the weight of *one atom—provided that the weights observed in other compounds are very nearly whole multiples of the least weight.*

An example will make the method clear. To find the atomic weight of chlorine we obtain a sample of each of a number of different compounds of chlorine, and determine (1) the approximate molecular weight of each, and (2) the percentage of chlorine in each:

	Approx. Molecular Weight *	*Percentage of Chlorine*	*Approx. Wt. of Chlorine in Molecular Weight*
Chlorine gas (uncombined)	72.0	100	72.0
Hydrogen chloride gas	36.7	97.3	.....
Chloroform vapor	121.6	89.0	108.2
Methyl chloride vapor	51.7	70.2	.....
Carbon tetrachloride vapor	156.2	92.4	144.3
Nitrosyl chloride	66.0	53.8	.....
Chlorine monoxide	87.0	81.6	71.0

(Similarly for dozens of other chlorine compounds)

* These are actual experimental figures, obtained by weighing the gas or vapor, in comparison with oxygen, under identical conditions.

Now let the reader calculate the weight of chlorine in one molecular weight, for each of the three substances in which this still remains to be done (last column of the table just given). The *least* of the weights so found is assumed to be the *least possible* weight of chlorine in any molecule, namely, one atomic weight of chlorine, provided that it divides very nearly evenly into other weights of chlorine, in one molecule of other compounds. The least weight turns out to be approximately 35.5 or 36; this is contained very nearly an even 1, 2, 3, and 4 times in the weight of chlorine in a molecule of other compounds of chlorine (last column in table). Thus 35.5 or 36.0 is the atomic weight of chlorine, approximately.

Atomic weights deduced as just described are only approximate, since in deriving them we have used molecular weights that are only approximate. (Ex. 9–12.)

Some Approximate Atomic Weights

Hydrogen	H	1	Sodium	Na	23	Calcium	Ca	40
Carbon	C	12	Aluminum	Al	27	Iron	Fe	56
Nitrogen	N	14	Sulfur	S	32	Copper	Cu	63.5
Oxygen	O	16	Chlorine	Cl	35.5	Mercury	Hg	200

The method for determining approximate atomic weights that has just been described is easy to understand. But it calls for so much labor from chemists who practice it that it deters all but the rare geniuses who have infinite capacity for taking pains. To determine the atomic weight of a single element, chlorine, for example, many compounds of the element needed to be *prepared*, then laboriously *purified*. Then the *molecular weight* of every one of them needed to be determined. Then every one of them needed to be carefully *analyzed*, often by methods which had to be specially invented, to determine its exact percentage of chlorine.

Only then was it possible to calculate *the least weight of chlorine ever encountered in a molecule of any chlorine compound*. This was presumably the *atomic weight* of chlorine. Anyone can see that the task of finding it might have called for several years of the working time of some chemist.

The method just described obviously cannot be used in finding the atomic weights of the *inert gases*, since these form no stable compounds. Instead, an indirect method is used (§ 121).

34. Exact Atomic Weights Based on Chemical Analysis

Approximate atomic weights, derived as just described, are sufficiently nearly exact to give correct chemical formulas. For example, the formula of potassium chlorate, as we shall presently see (§ 40), turns out to be $KClO_3$, even though somewhat inexact atomic weights are used in finding it. This formula means that for every atom of potassium in this compound there are one atom of chlorine and three of oxygen.

Then, *by reviewing the precise analysis of some compound, in the light of its known formula*, it is possible to obtain the exact atomic weight of some element contained in it. For example, the precise analysis of potassium chlorate shows that it contains 35.46 weight units (grams or pounds) of chlorine for every 48 weight units (grams or pounds) of oxygen. The 48 weight units account for the three atoms of oxygen in the formula $KClO_3$; then 35.46 must represent the one atom of chlorine in the formula, hence must be the exact atomic weight of chlorine. (Ex. 13.)

35. The Mass Spectrograph Reveals Isotopes

About 1920, a surprisingly simple *physical method* was developed, which first supplemented, then largely superseded, the tedious indirect *chemical method* for determining exact atomic weights. It determines

the relative weights of atoms directly, using an instrument called the mass spectrograph (Fig. 6).

Atoms of an element to be tested are given electrical charges by methods that need not be described. Then a swarm of such atoms, *all moving with the same speed*, are passed through the field of a powerful

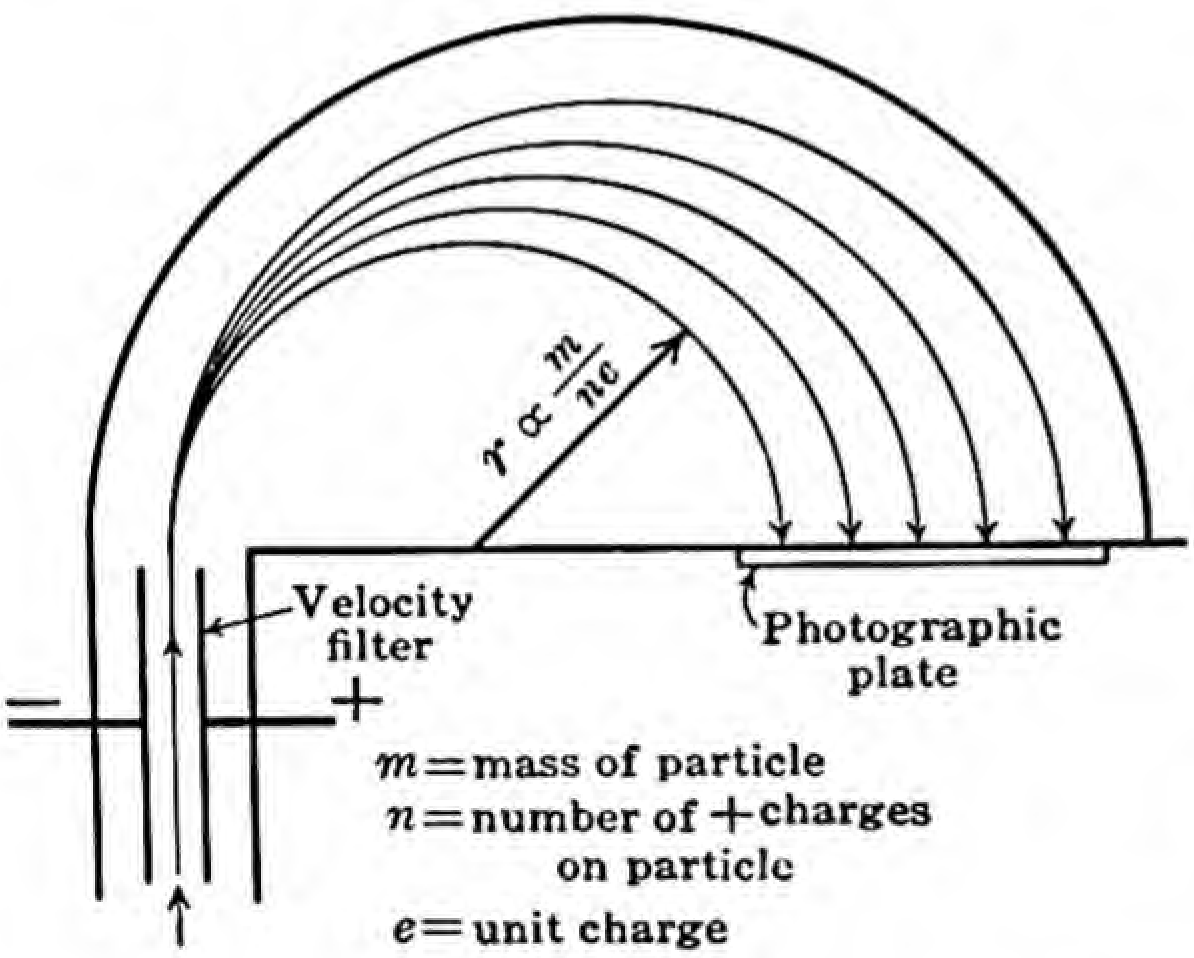


FIG. 6. Diagram of the Bainbridge mass spectrograph. Only particles within a definite, very small range of velocity get through the velocity filter, which consists of two parallel, oppositely charged plates. The particles then follow curved paths, in traversing a magnetic field. All particles having any given ratio of charge to mass follow the same path and register at the same spot on the photographic plate.

magnet. This acts upon the electrical charges carried by the atoms, deflecting the atoms into curved paths which approximate the arcs of circles. Now observe: *The heavier an atom* (of any given electrical charge) *the farther out it will swing*, as it traverses the magnetic field. So a photographic plate is placed where the moving atoms will strike it. The heavier they are the farther to the right they will strike in Fig. 6. The atoms themselves are of course invisible, but the places where they strike are registered on the photographic plate, and appear as a series of dark spots (Fig. 7) when the plate is developed.

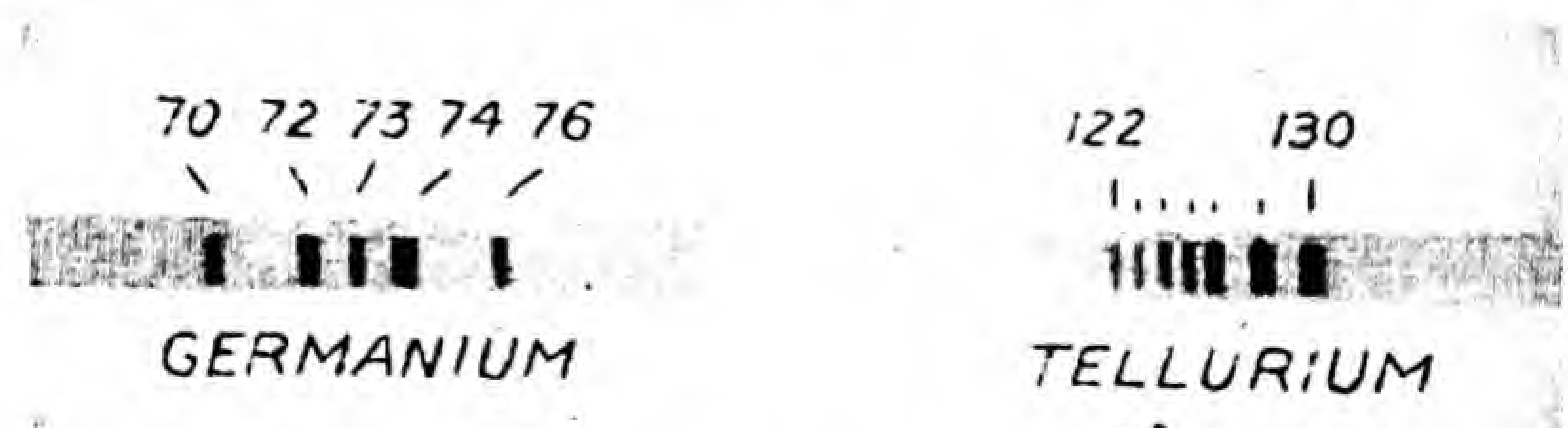


FIG. 7. Spots representing different isotopes of germanium and tellurium, registered on the photographic plate of a mass spectrograph.

One may illustrate the principle of the mass spectrograph by whirling a number of balls of different weights, one after another, at the end of the same rubber cord. If you whirl them all at the same speed you will discover that the heavier a ball is the more it will stretch the rubber cord, and the farther out it will strike against a sheet of

cardboard that is suddenly interposed (to represent a photographic plate).

Data obtained with the mass spectrograph disclosed a very surprising fact: *Only a few elements* (fluorine, aluminum, phosphorus, for example) *exist in nature as atoms that are all of the same mass.* Even for these elements, atoms of other than the usual mass have been produced artificially, from other elements. In every instance, they have proved to be unstable, *decomposing*, after a short or long period (§ 587).

Forms of an element which differ in atomic mass are called *isotopes.* In spite of the difference in atomic mass, *the different isotopes of an element are almost or quite completely identical in their chemical properties.* Most elements are mixtures of several different isotopes. A few of them (tin, mercury, lead, for instance) contain eight to ten isotopes.

Hundreds of different isotopes, for the 96 elements now known, have been identified in nature, and hundreds of others (both stable and unstable) have been created artificially.

36. International Atomic Weights

Now let us see how data obtained by the mass spectrograph may be used in determining atomic weights. The *distance* of any spot on the photographic plate from a reference point near one edge of the plate permits us to calculate the relative mass of an atom of the type that produced that spot. The *relative blackness* of any spot is a good indication of the relative number of atoms which reached that point. So we have all the data needed for finding the average mass of the several sorts of atoms that compose any given element. This *average isotopic mass* (when reduced to the scale that makes the average for oxygen an even 16 units) is the *atomic weight* of the element. (Ex. 14, 15.)

Atomic weights obtained directly with a mass spectrograph are in close agreement with those found by the indirect chemical method. When there has been disagreement the chemical method has always been found to be slightly in error. Anyone with skill in the use of the instrument can determine the atomic weight of an element within a few hours, and even with samples of material that are too impure to be of any use by the chemical method. So our admiration for the patient labors of Stas, a Belgian chemist (1813–1891), who devoted nearly twenty years to establishing atomic weighs precisely by the chemical method, is mingled with regret that the mass spectrograph had to await the twentieth century.

In times of peace an international committee constantly reviews current researches that may seek to obtain atomic weights of increased precision. The values which this committee considers most reliable are included in a table of *International Atomic Weights* (facing the front cover of this book). The student should examine this table to determine whether or not atomic weights of different elements all appear to have been determined with the same *order of precision* (as indicated by the number of *significant figures* to which the different values have been expressed).

Before leaving this topic the reader should be sure to note one further point: *The atomic weight of an element has rarely been found to vary in the least with the geographical source of the element.* For example, chlorine from salt obtained from a deposit in New York has the same atomic weight as chlorine extracted from a mineral mined in Australia. In brief, *the isotopes of any element are almost always intermingled in unvarying proportions, no matter where we may find the element.*

We may conclude that the atoms that compose the earth were pretty thoroughly mixed before the earth came into being. Since the isotopes of any given element are nearly or completely identical in their chemical properties, the chemical events that gave us separate ore deposits of the different *elements* did not separate *isotopes.*

37. Chemical Symbols

The alchemists represented the different materials known to them by arbitrary symbols, including some that are still in use in almanacs to represent the chief planets, which in alchemical times were identified with the best known metals. The alchemical symbols ♂ and ♀, which originally represented iron and copper and the planets Mars and Venus, still appear in biology, in connection with discussions of inheritance, as symbols for *male* and *female.* The alchemists took what seems today to be an unnecessary precaution in employing secret symbols to *prevent* science from being too easily understood by everyone.

Dalton represented atoms by marked or initialed circles, as in § 25. A better system, introduced by the Swedish chemist Berzelius in 1813, represents each element (more precisely, *one atom of each element*) by a *chemical symbol,* consisting of the initial letter or a pair of letters of the Latin name of the element. The only symbols not also suggested by the English name of the element are the following, which should be memorized now:

Antimony (*stibium*)........	Sb	Mercury (*hydrargyrum*).....	Hg
Copper (*cuprum*)..........	Cu	Potassium (*kalium*)........	K
Gold (*aurum*)..............	Au	Silver (*argentum*)...........	Ag
Iron (*ferrum*)..............	Fe	Sodium (*natrium*)..........	Na
Lead (*plumbum*)...........	Pb	Tungsten (*wolframium*).....	W

Symbols for a few other common elements, which might as well be memorized now, are given on p. 34.

38. Chemical Formulas for Elementary Gases

Now let us compare the molecular weights of a few elements with their atomic weights. The molecular weight of gaseous oxygen is 32; its atomic weight is 16. Thus *a molecule of gaseous oxygen contains two atoms.* The same is true of hydrogen, nitrogen, chlorine, bromine, iodine, and a number of other elements, in the state of a gas or vapor, at ordinary temperatures. Since the symbol of an element represents a single atom, a molecule of each of the elements just named, in the gaseous state, at ordinary temperatures, must be represented by a double symbol, for example, by H_2, O_2, N_2, Cl_2, Br_2, I_2. These are the chemical formulas of the given elements, as we ordinarily encounter them. We thus perceive a fact which escaped Dalton and his successors, during nearly half a century; *even an element may exist as compound atoms, now called molecules, and not necessarily as simple atoms.* A molecule containing two atoms is a *diatomic* molecule.

The double atoms (molecules) just listed are decomposed, at sufficiently high temperatures:

$$I_2 \rightleftharpoons 2I$$

We here indicate that a molecule, containing two atoms, can be made to yield two separate molecules, each containing one atom. This shows very plainly that *the number of atoms in a molecule of an element, and hence the molecular weight of the element, often depend on the temperature and other conditions under which the element is observed.* A few elements (metallic vapors and the inert gases, § 121) have but a single atom in the molecule at all temperatures. (Ex. 16–18.)

To repeat and reemphasize: an individual *atom* of an element is always represented by a *symbol* (H, O, N, etc.); a *molecule* is represented by a *formula* (H_2, O_2, N_2, I_2; or He, Ne, A, Hg, I) which tells how many atoms compose the molecule, under stated conditions. We see that the symbol and formula of an element are identical whenever a molecule of the element happens to contain only one atom.

39. Deriving the Formula of a Compound

We have just deduced formulas for some common elements. Next, let us turn to compounds. When we have drawn up a list of approximate atomic weights and molecular weights, as already described, the rest is easy. We have seen (last column of table, p. 34) that the weight of chlorine in a molecular weight of chloroform is very nearly three times the least weight of chlorine ever encountered in any molecular weight, in other words, is three times the atomic weight of chlorine. Evidently a molecule of chloroform contains three atoms of chlorine. Similarly a molecule of chloroform may be shown to contain one atom of carbon and one atom of hydrogen. It is therefore represented by the chemical formula $CHCl_3$. In brief, *to derive the formula of any substance we need only note what multiple of the atomic weight of each element is contained in one molecular weight of the substance.* (Ex. 19–24.)

40. Deriving an Empirical Formula

Let us next derive a formula for potassium chlorate. This substance does not consist of molecules, but of electrically charged atoms or groups of atoms, called *ions*, discussed hereafter. So it has no molecular weight, in the ordinary sense. But very careful determination of the percentage of each element in it gives the results shown in the first column of figures in this table:

	Per Cent	*Weight Units for 16 Weight Units of Oxygen*	*Atoms of Each Element*
Potassium	31.90	13.032	$\frac{1}{3}$
Chlorine	28.93	11.819	$\frac{1}{3}$
Oxygen	39.17	**16**	**1**

The second column of figures is obtained by multiplying all those in the first column by 16/39.17, thus reducing the weight of oxygen to an even 16 units (the standard of atomic weights) and reducing the weights of all the other elements in the same proportion.

Now let us suppose that the atomic weight of potassium is known to be roughly 39 and that of chlorine to be roughly 35.5. Even these *rough values* permit us to see that in the second column of figures we have very nearly one-third atom of potassium, one-third atom of chlorine, and one atom of oxygen. (There are fractional atoms be-

cause we did not know the molecular weight of the compound.) The smallest multiplier that will convert all these fractions into whole numbers is three. So, multiplying by three, we see that the three elements are in the ratio of one atom of potassium and one atom of chlorine for every three atoms of oxygen. Therefore potassium chlorate must be represented by the formula $KClO_3$.

A formula which merely represents the *simplest possible formula* for a compound and does not indicate its molecular weight (because the molecular weight is undetermined or indefinitely large, or because the substance consists of ions rather than ordinary molecules) is called an **empirical** or **conventional formula.** A formula which does indicate the molecular weight of a compound is called a **molecular formula.**

The reader will learn by experience which chemical formulas actually represent molecules and which merely indicate relative numbers of atoms or ions in a crystal or solution. As a rough guide:

Molecular formulas: gases and vapors; liquids and solids that happen to be readily vaporized.

Empirical formulas: most other substances, including nearly all minerals and most salts (common salt, NaCl, for example). (Ex. 25.)

41. Formula Weights

When the formula of a substance has been determined, we may find the corresponding *formula weight* by adding indicated multiples of atomic weights, taken from a table. Thus for chloroform, $CHCl_3$:

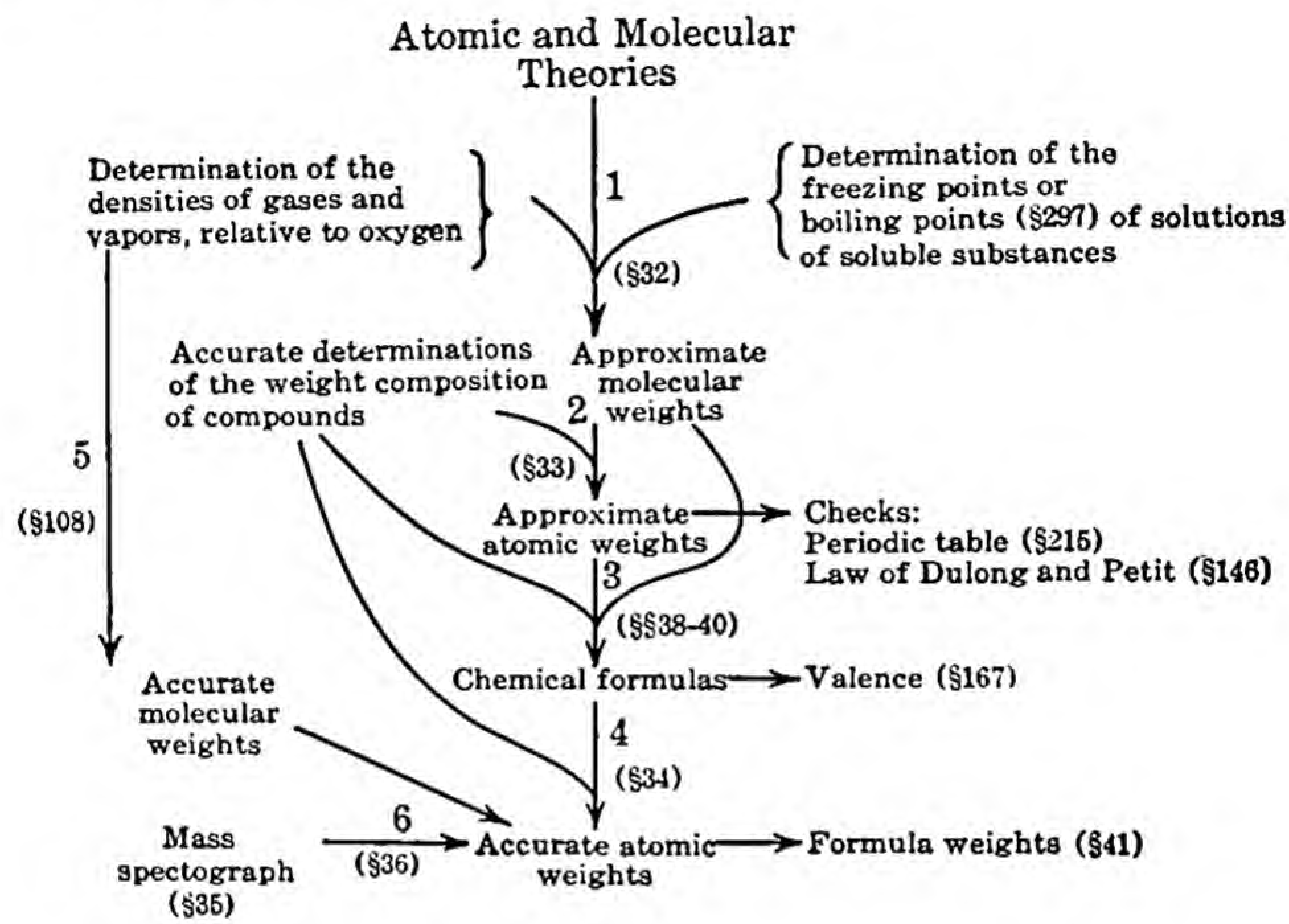
$$\begin{aligned} C &= 12.01 \\ H &= 1.0078 \\ Cl_3 = 3 \times 35.457 &= \underline{106.371} \\ \text{Formula weight for } CHCl_3 &= 119.3888, \text{ rounded to } 119.4, \text{ parts by weight} \end{aligned}$$

The formula weight of a substance is the same as its molecular weight whenever the formula actually represents a molecule (as happens to be true of chloroform). For substances represented by *empirical formulas* (quartz and common salt, for example) there is, strictly speaking, only a formula weight and no definite molecular weight.

When we write $CHCl_3$ we mean *one molecule* of chloroform. Two molecules would be written $2CHCl_3$, not $C_2H_2Cl_6$.

42. Summary

This chapter is so important that the student should review it carefully, with the aid of the following diagram.



TECHNICAL WORDS

Molecular weight, p. 32. **Atomic weight,** p. 32.

Ionic weight. This term is left to the student to define.

Chemical symbol, p. 38. **Chemical formula,** p. 39.

Formula weight—the sum of the atomic weights indicated by a formula.

Conventional formula, molecular formula, p. 41.

Mass spectrograph, p. 36. **Isotope,** p. 37.

Monatomic, diatomic, triatomic—containing respectively one, two, or three atoms in a molecule.

SUMMARY

§ 30. Are atomic and molecular weights compared with the same unit of weight? What is it?

§ 31. State and illustrate the principle of Avogadro.

§ 32. How may we find the molecular weight of a gas by weighing it, then comparing this weight with another?

§ 33. Indicate steps to determine the approximate atomic weight of an element.

§ 34. Explain how we may pass from approximate to accurate values of atomic weights.

§ 35. How do the particles observed with a mass spectrograph differ from ordinary atoms? Why do they move in curved paths?

§ 36. Explain (p. 28) how mass is related to weight. Explain how an atomic weight may be derived from data obtained with the mass spectrograph.

§ 37. Who introduced the modern system of chemical symbols? On what language are these symbols really based?

§ 38. Explain how we know that a molecule of gaseous oxygen contains two atoms. Indicate some other elements for which this is true.

Distinguish between symbol and formula.

§ 39. If we know the molecular weight of a substance and its percentage composition by weight, what else must we know to arrive at its formula? Explain how the formula is then derived.

Illustrate for a compound of molecular weight 34, which is $\frac{1}{17}$ by weight hydrogen, the remainder sulfur. How would you represent three such molecules?

§ 40. What information is lacking for potassium chlorate that we possess for chloroform, as an aid to determining a formula?

For what reasons may substances be of indefinite molecular weight?

Distinguish between molecular and conventional formulas, and tell what sorts of substances are represented by each.

§ 41. Explain what is meant by a formula weight. When is the formula weight identical with the molecular weight of the substance?

§ 42. Reproduce from memory the diagram summarizing the course of reasoning in deriving chemical formulas and accurate atomic weights. Explain one or two steps in the reasoning.

Exercises

1. A molecule of sulfur dioxide has been shown to be twice as heavy as a molecule of oxygen. What is the molecular weight of sulfur dioxide? 640

2. What is the molecular weight of a substance, each molecule of which is formed by the direct union of a molecule of carbon monoxide (molecular weight, 28) with an atom of oxygen? 440

3. A nitrogen molecule weighs only $\frac{7}{8}$ as much as a molecule of oxygen. Find the average molecular weight of the gases in a mixture (air) that contains four molecules of nitrogen for each molecule of oxygen. 288

4. If a liter of oxygen weighs 1.43 grams, what will be the weight, under the same conditions, of a liter of another gas having a molecular weight of 64? 286

5. A liter of oxygen weighs the same as 2 liters of methane. How does the molecular weight of methane compare with that of oxygen? 500

6. What is the molecular weight of a gas having twice the density of oxygen?

7. What volume of a gas of molecular weight 48 has the same weight as 3 liters of oxygen, under the same conditions? 200

8. The average molecular weight of the gases of the air is about 29. Is oxygen heavier or lighter than air?

9. The weights of a certain element in one mole of each of a number of different compounds are 28, 42, 70, and 84. Explain (italics, § 33) why the least of these figures may not be taken as the atomic weight of the element. Show that half of it could be so taken.

10. The least weight of calcium in a molecular weight of any calcium compound is $2\frac{1}{2}$ times the least weight of oxygen in a molecular weight of any oxygen compound. What is the approximate atomic weight of calcium? 400

11. Ammonia gas contains three times as much hydrogen as is contained in an equal volume of hydrogen chloride. Moreover, no gaseous compound of hydrogen contains less hydrogen than is found in an equal volume of hydrogen chloride. What conclusions may be drawn?

12. The following table gives the approximate molecular weight of each of a number of different compounds of carbon, and the percentage of carbon in each. Calculate the approximate weight of carbon in a molecular weight of each, and select from the figures so obtained the one that represents the approximate atomic weight of carbon:

	Approx. Mol. Wt.	*Per Cent Carbon*	*Approx. Wt. of Carbon in 1 Mol. Wt.*
Carbon monoxide	28	42.9	
Ethylene	28	85.7	
Propane	44	81.8	
Butane	58	82.8	
Benzene	78	92.3	
Carbon dioxide	44	27.3	

13. Potassium perchlorate has the formula $KClO_4$. It contains 1.1026 parts by weight of potassium for each part by weight of chlorine. If the exact atomic weight of chlorine is 35.457, what is that of potassium? 391

14. Chlorine consists of about twenty-four atoms of isotopic mass 37 for every seventy-six of isotopic mass 35. Find the total mass of these hundred atoms. Then find their average mass, to four significant figures. This is the atomic weight of chlorine.

15. The three isotopes of magnesium have the relative masses 24, 25, 26. The relative blackness of the corresponding spots on a mass spectrograph film indicates that the first isotope is about 7 times as abundant as either of the others. Find the atomic weight of magnesium. 243

16. Sulfur vapor, at temperatures just above the boiling point of that element, is 8 times as heavy as an equal volume of oxygen at the same temperature. What is the approximate molecular weight of the sulfur vapor, under these conditions? Comparing with the *atomic weight* of sulfur, deduce the formula of sulfur vapor.

17. If the molecules, H_2, of ordinary hydrogen could be decomposed into simple monatomic molecules, H, without changing the temperature, what would this do to the total number of molecules? What would happen to the volume occupied by the gas?

18. The density of a certain elementary vapor is 5 times that of oxygen at the same temperature. If its molecules are diatomic, what is its atomic weight? 800

19. In Exercise 12 we determined the approximate atomic weight of carbon. Compare this with the calculated weight of carbon in one molecular weight of each of the six compounds listed, to deduce how many atoms of carbon are present in one molecule of each.

20. The weight of a liter of a certain vapor is 2.375 times that of a liter of oxygen, at the same temperature This substance contains 15.80 per cent carbon, and the rest sulfur. Calculate the weight of each element in one molecular weight of the compound, then compare with the approximate atomic weights, to deduce the formula of the compound. 120, 640

21. Explain how it has been proved that the formula of chlorine is Cl_2.

22. A certain compound contains 1.26 per cent hydrogen, 38.78 per cent phosphorus, and the rest oxygen. Assuming a molecular weight of 80, calculate a formula.

23. The vapor of a certain liquid is known to be about twice as heavy as air. What is its approximate molecular weight, if the gases contained in air have an average molecular weight of 29? 580

If this liquid contains 62.02 per cent carbon, 10.42 per cent hydrogen, and 27.56 per cent oxygen, what is its formula?

24. Water vapor contains 11.19 per cent hydrogen and the rest oxygen. It is 0.562 times as dense as oxygen, under the same conditions. Deduce its formula.

25. Ferric oxide contains 70 per cent iron and the rest oxygen. How many weight units of iron are present for every three atoms of oxygen? Compare with the atomic weights of these two elements to deduce an empirical formula for ferric oxide.

26. Calculate the formula weight of acetone, $(CH_3)_2CO$. (The 2 multiplies everything within the parentheses.) 580

27. Calculate the formula weight of glycerol, $C_3H_5(OH)_3$. 920

28. How many molecules and how many units of weight are represented by $5CO_2$?

29. Which represents the greater weight of material, $2SO_2$ or $5O_2$?

30. Which has the greater total weight, 10 liters of acetone vapor, $(CH_3)_2CO$, or 5 liters of chloroform vapor, $CHCl_3$, under the same conditions?

Chapter 5

OXYGEN

Our discussion of typical chemical changes may well begin with those involving oxygen, the most abundant element.

43. Occurrence of Oxygen

Elementary (that is, *free* or *uncombined*) oxygen makes up a little more than one fifth of the air (by volume or by weight).

Combined with other elements, oxygen is found:

1. In a large part of the stony *minerals* and *soils* of the earth's crust. Most of them are about half oxygen, by weight.

2. In *water*. This is about eight-ninths oxygen and one-ninth hydrogen, by weight.

3. In *living plants* and *animals*. These contain not only water but also other oxygen compounds. Important examples are the vegetable and animal fats and oils, and cellulose (§ 467), which is the chief ingredient of cotton, linen, and rayon, and which makes up about half of most woods.

44. Preparation of Oxygen

Since oxygen, in the materials just mentioned, is *chemically combined* with other elements, it is difficult or impossible to obtain it from them in a pure condition:

1. *Air*, however, is a mere *mixture* of oxygen with about 4 times its own volume of nitrogen and smaller amounts of other gases. To separate these gases the air is liquefied. Then, by controlled evaporation, the nitrogen passes off first, leaving nearly pure oxygen behind. This is the chief source of oxygen for industrial uses (§ 62).

2. *Water*, alone of the oxygen compounds abundant in nature, can be decomposed in any convenient way. When an electric current is passed through water, it is decomposed into hydrogen and oxygen (§ 45, item 5). Both these gases are sometimes prepared commercially in that way.

3. *A few substances rich in oxygen yield pure or nearly pure oxygen on being strongly heated.* *Potassium chlorate* (a white crystalline solid) is the most convenient of these.

4. *Sodium peroxide* (mixed with cupric oxide) will yield oxygen *on being moistened with water.* It should not be heated.

45. Lecture Demonstration

Preparation of Oxygen on a Small Scale in the Laboratory

Topics best introduced by demonstrations will be presented hereafter as brief summaries, to be amplified by the student from his lecture notes.

1. *Potassium chlorate,* strongly heated, yields oxygen, and leaves a residue of *potassium chloride.* Sodium chlorate, similarly, yields sodium chloride.

If the chlorate is mixed with a little manganese dioxide, the oxygen is set free more rapidly and at a lower temperature (Fig. 8) than is otherwise possible. This is our

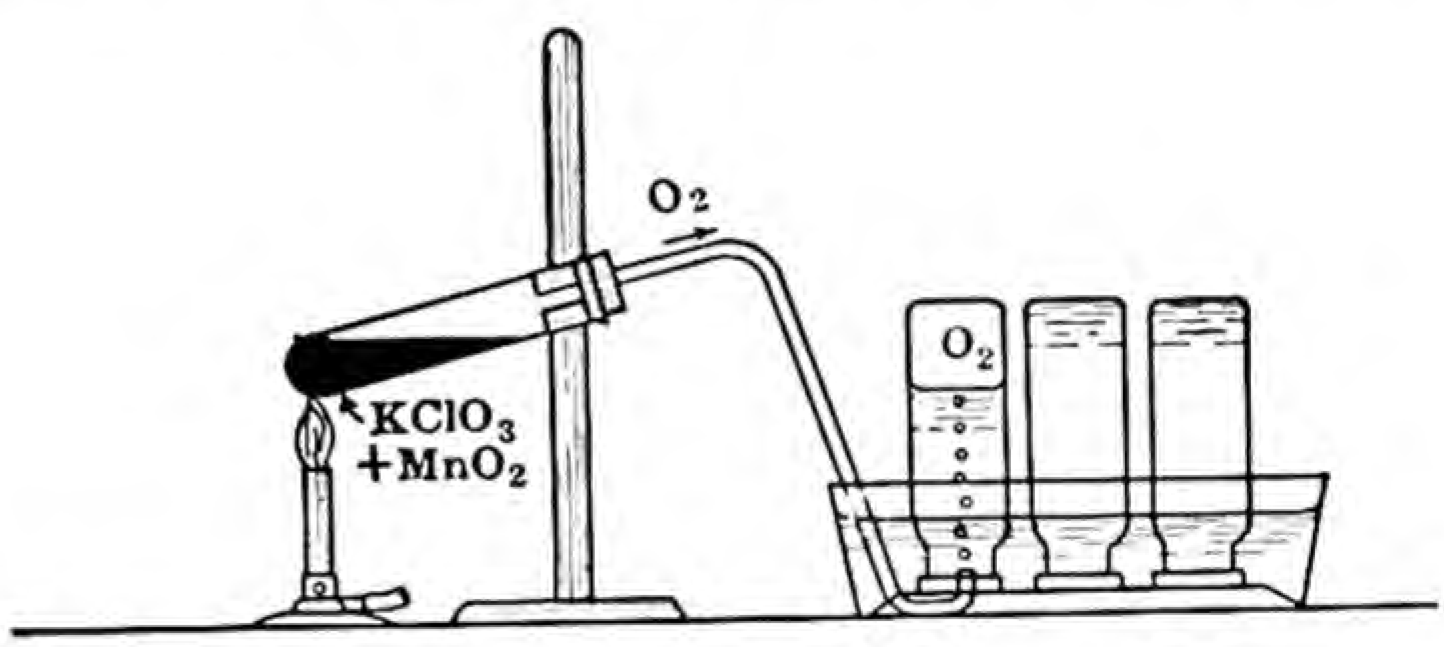


FIG. 8. Preparation of oxygen.

first example of a *catalyst*—a substance that *increases* (or sometimes *decreases*) the rate of a chemical transformation, without itself being permanently altered chemically. In brief:

Potassium chlorate	$\longrightarrow$	Potassium chloride + Oxygen gas
White solid, nearly 40% oxygen	Catalyst, manganese dioxide	White solid, contains no oxygen

This is a reaction summary. The arrow is read "yields" or "produces"; the plus sign is read "and."

Test for oxygen: A spark at the end of a wooden splint bursts into flame when the splint is thrust into gaseous oxygen.

2. Oxygen may also be prepared by strongly heating *potassium nitrate:*

Potassium nitrate	$\longrightarrow$	Potassium nitrite + Oxygen gas
White solid, nearly 50% oxygen		White solid, about 30% oxygen

3. The *noble metals* (silver, mercury, gold, platinum) can be made to combine with ordinary oxygen only with difficulty, or by indirect means too complicated to describe here. (The tarnishing of silver is ordinarily not oxidation, but formation of silver sulfide.) If by indirect means we do succeed in preparing *oxides of the*

noble metals, we find that these are easily decomposed on being heated, leaving the metal behind:

Mercuric oxide	→	Mercury	+	Oxygen gas
Red solid, about 7.5% oxygen		Silvery liquid, containing no oxygen		

4. *Sodium peroxide* (mixed with cupric oxide to serve as a catalyst) reacts with water, liberating oxygen. *Do not use hot water, or the reaction may be dangerously violent.*

Sodium peroxide	+	Water	→	Sodium hydroxide	+	Oxygen gas
Pale yellow solid, over 40% oxygen		Contains oxygen and hydrogen		White solid (remains dissolved); still contains half the oxygen of the peroxide		Comes from the peroxide, not the water

5. *Preparation of oxygen by electrolysis of water.* Apparatus commonly used as a lecture experiment is shown in Fig. 9. A little acid or alkali is usually added to the water to make it conduct better; but it is the water itself, and not the added substance, that is decomposed.

The decomposition of a material by the passage of an electric current through it is called *electrolysis*. The two conductors through which the electric current enters and leaves the liquid in which something is being decomposed by electrolysis are called the *electrodes*. The electrode (negatively charged) at which hydrogen is liberated is called the *cathode;* the electrode (positively charged) at which oxygen is liberated is called the *anode*.

Though the hydrogen set free occupies twice the volume of the oxygen it weighs only about one eighth as much.

Water (electrolyzed)	→	Hydrogen	+	Oxygen
		2 volumes		1 volume

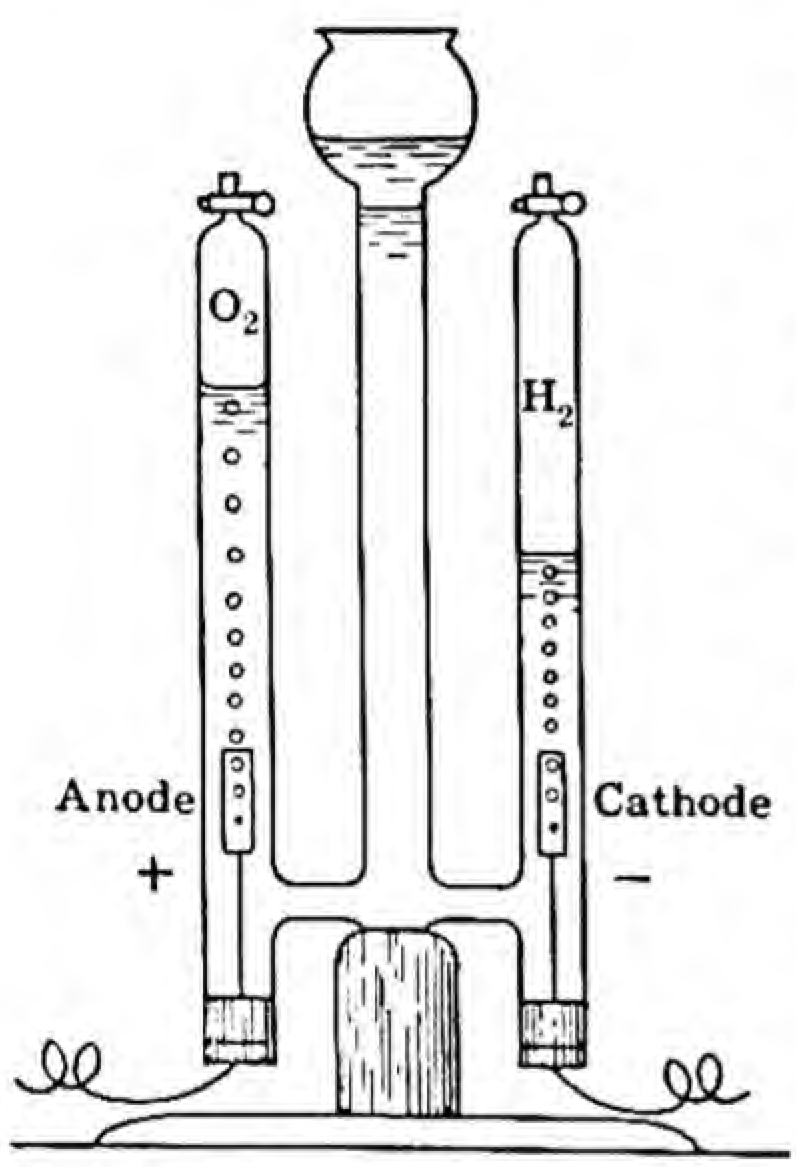


FIG. 9. Electrolysis of water.

6. *Physical properties of oxygen* (§ 51).

46. Writing a Chemical Equation

The preparation of oxygen from potassium chlorate has been summarized:

$$\text{Potassium chlorate} \rightarrow \text{Potassium chloride} + \text{Oxygen}$$

Replacing names by the formulas of the three substances concerned:

$$KClO_3 \rightarrow KCl + O_2 \qquad \text{(unbalanced)}$$

A chemist would criticize this *formulation*, saying that it is *unbalanced.* By this he means that three atoms of oxygen appear in the formula of potassium chlorate, but only two of these are accounted for in the formula of oxygen. We cannot correct this by altering O_2 to O_3, for a

molecule of ordinary oxygen actually contains two, and not three, atoms. The three atoms of oxygen in the formula of potassium chlorate can evidently yield one and one-half molecules of ordinary gaseous oxygen, namely $1\frac{1}{2}O_2$. Accordingly we may write:

$$KClO_3 \rightarrow KCl + 1\tfrac{1}{2}O_2$$

To avoid the use of a fractional part of a molecule, take twice the quantities just indicated, and thus obtain:

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

This is a balanced formulation, commonly called a *chemical equation*. It is read: "Two formula weights of potassium chlorate yield two formula weights of potassium chloride and three formula weights of oxygen." (Potassium chlorate and potassium chloride exist as positively and negatively charged ions, rather than as molecules.)

47. Another Example

In preparing oxygen from sodium peroxide, let us represent the reactants and resultants by their formulas. Thus we obtain the formulation

$$\underset{\text{Sodium peroxide}}{Na_2O_2} + H_2O \rightarrow \underset{\text{Sodium hydroxide}}{NaOH} + O_2 \qquad \text{(unbalanced)}$$

This is still to be balanced. As a suggestion worth remembering: *Begin by balancing elements that occur only once on each side of the equation.* Sodium and hydrogen fulfill this requirement in the preceding equation, but oxygen does not; hence we put off balancing the oxygen until the two former elements have been adjusted. First we notice that the two sodium atoms in Na_2O_2, on the left, call for 2NaOH on the right. Hydrogen then balances (two atoms on each side of the equation). Thus we have settled the proportions of three of the four substances appearing in the equation. Only oxygen gas remains to be adjusted, by writing $\frac{1}{2}O_2$ on the right. This gives three oxygen atoms on each side of the equation. By doubling the equation we then obtain

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

(Ex. 1–3.)

48. A Hint to the Student

Do not attempt to memorize equations. The important thing is to remember, for each important reaction, (1) the names of the reacting

substances, (2) the names of the products obtained from them, and (3) the conditions under which the reaction takes place. As examples of conditions remember whether the reactants are intermingled in the solid state or first dissolved in water; or perhaps whether one of them, in the gaseous state, is passed over or through the other. Remember whether the material to be transformed needs to be heated to bring about the transformation, whether a catalyst is needed, and if so what catalyst serves best.

Anyone who knows this much about a reaction may readily translate the names of reactants and resultants into chemical formulas (at first memorized, one by one, as they are encountered, but later often derived as needed with the help of some general rules, § 169). The *formulation* thus obtained may then often be balanced by a simple inspection, in which fractional parts of molecules are often useful as intermediate steps.

Equations that are very difficult to balance may be left in the unbalanced form until special rules for balancing have been discussed. Indeed some instructors prefer to postpone balancing until some later part of the course, in order to lay emphasis at first on *the conditions under which the reactions take place*, and *the identity of reactants and resultants.* To indicate that a formulation has been left in the unbalanced form the symbol > may be used as a substitute for an arrow.

49. Three Meanings for a Chemical Equation

Properly balanced, an equation shows not merely (1) the *names* of the substances originally present (reactants) and the names of those produced (reaction products or resultants), but also (2) the *relative number of molecules or ions* of each, and (3) the *relative weights* of each.

Thus the balanced equation for the preparation of oxygen from potassium chlorate

$$\underset{\text{245 weight units}}{2KClO_3} \rightarrow \underset{\text{149 weight units}}{2KCl} + \underset{\text{96 weight units}}{3O_2} \qquad \text{Check: } 149 + 96 = 245 \text{ weight units}$$

indicates that 2 formula weights of potassium chlorate, when decomposed, yield 2 formula weights of potassium chloride and 3 formula weights of oxygen gas. Using rounded atomic weights (table facing front cover), we find that $2KClO_3$ represents approximately $2 \times (39 + 35.5 + 48) = 245$ weight units. This, when completely decomposed, yields $2KCl$ and $3O_2$, that is, $2 \times (39 + 35.5) = 149$ weight units of potassium chloride, and $3 \times 32 = 96$ weight units of

oxygen. (Check these figures.) These weight units may be grams, ounces, tons, or any other weight units we please, since we are concerned, after all, only with definite *relative* weights (Law of Definite Proportions, § 23). (Ex. 4–6.)

The figures just given permit us to calculate the percentage of oxygen in potassium chlorate. For if 245 parts by weight of that substance yield 96 parts by weight of oxygen, it is plain that oxygen must make up 96/245 of the total weight. Expressed as a decimal fraction, this is 0.392, namely, 39.2 per cent. (Ex. 7, 8.)

50. Another Example

If we inquire what weight of oxygen will be obtained from any given weight of sodium peroxide, the balanced equation

$$\underset{\text{156 weight units}}{2Na_2O_2} + 2H_2O \rightarrow 4NaOH + \underset{\text{32 weight units}}{O_2}$$

gives us the answer. For 2 formula weights of the peroxide, that is, $2Na_2O_2$, represent a total of $2 \times (46 + 32) = 156$ weight units. These 156 weight units yield O_2, which represents 32 weight units of oxygen. In brief, the oxygen weighs 32/156 as much as the peroxide from which it comes. If we had 5 pounds of sodium peroxide we should get 32/156 of 5 pounds = 1.03 pounds of oxygen. The method would, of course, be the same if weights were in grams, ounces, tons, or any other weight units. (Ex. 9–11.)

51. Physical Properties of Oxygen

Important physical properties for distinguishing one gas from another are *color*, *odor*, *ease of liquefaction*, *density*, and *solubility*.

Oxygen is a colorless, odorless gas, which is liquefied only under high pressures, at temperatures far below the freezing point of water. The *critical temperature* of oxygen, namely, the highest temperature at which it is possible to liquefy it at all, is $-118°C$. This is 212 degrees, on the Fahrenheit scale, below the freezing point of water! At this temperature the pressure necessary to liquefy oxygen is about 50 atmospheres, or about 745 pounds per square inch.

Oxygen weighs somewhat more than an equal volume of air, in other words, has a somewhat higher *density*. It is very slightly soluble in water (about 4 volumes of the gas dissolving in 100 volumes of water at room temperature).

52. Lecture Demonstration

1. *Combustion.* Burning or *combustion* is a vigorous reaction (usually one of direct union with oxygen), accompanied by emission of light and easily evident heat.

Many substances burn in pure oxygen that fail to burn in air (where the oxygen is diluted with 4 times its volume of a chemically inert gas, nitrogen). All substances that burn in air burn more rapidly in pure oxygen. Examples: burning phosphorus, sulfur, charcoal, and iron, in air and in pure oxygen. Observe the decrease

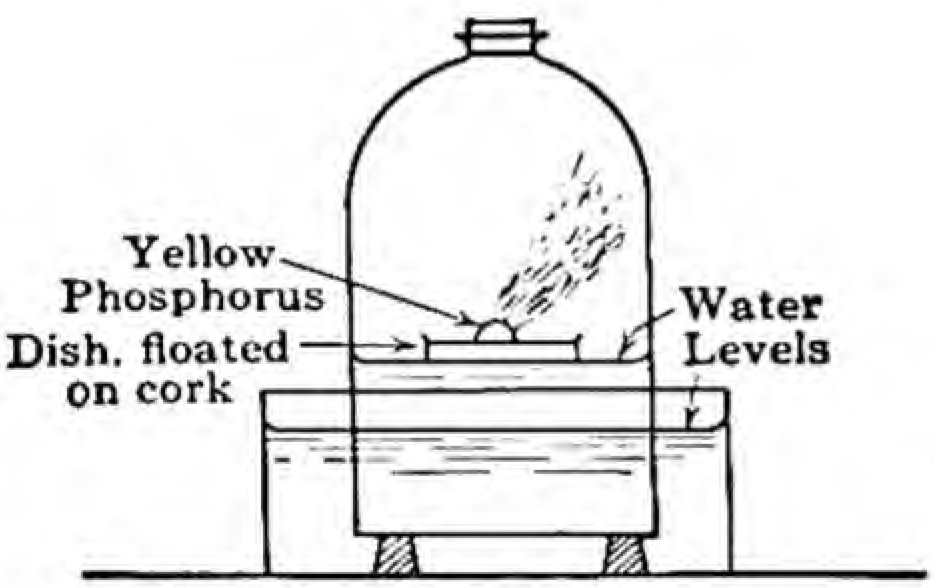


FIG. 10.

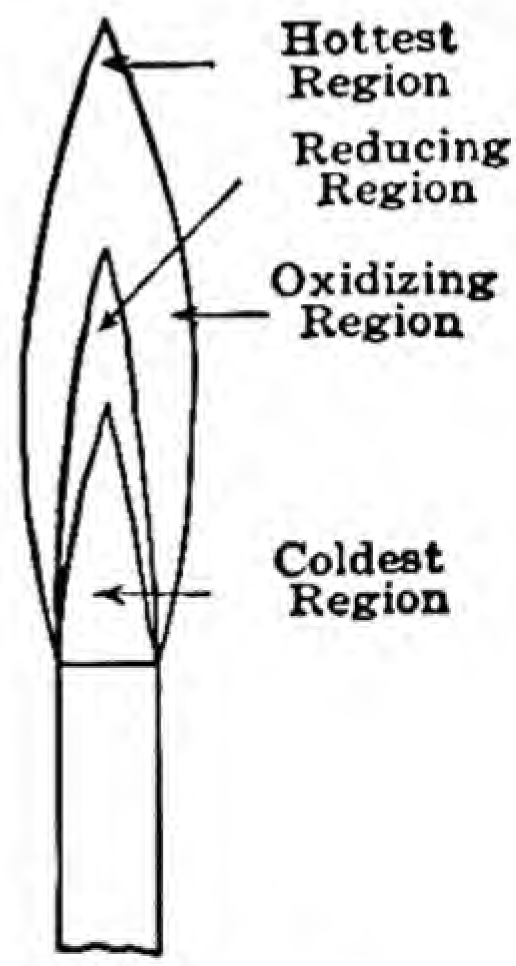


FIG. 11.

in volume that takes place when phosphorus burns under a bell-jar, over water (Fig. 10), or when iron filings, under a bell-jar, slowly rust.

2. *The Bunsen flame.* A flame is a zone of *incandescent* gas (gas so hot that it glows with visible light).

Different zones or regions in a Bunsen flame (Fig. 11): *Hottest region* at tip of flame; *coldest region* within inner cone . *Oxidizing region* near surface of flame (plenty of oxygen there, from surrounding air). *Reducing region* within flame, at top of inner cone (excess of gas here, and reasonably high temperature).

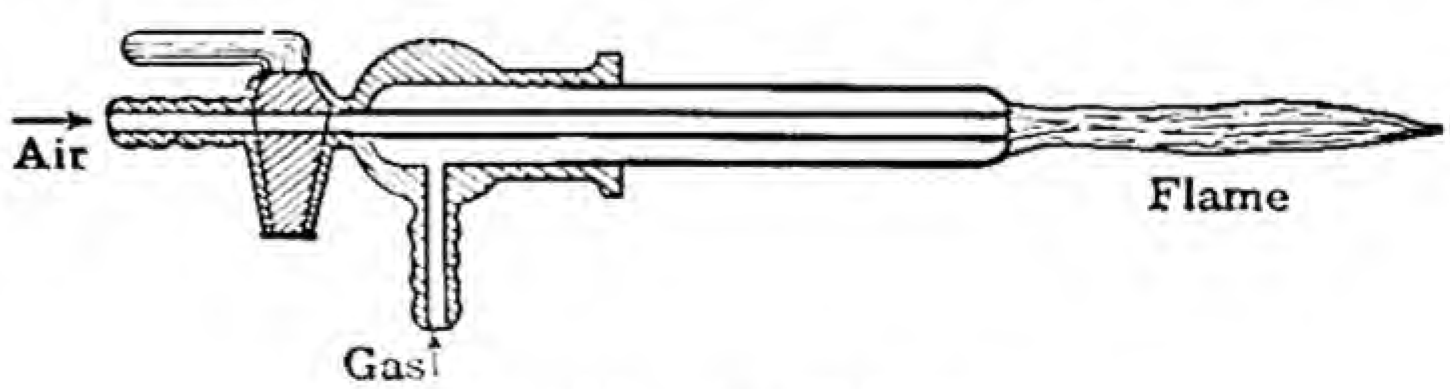


FIG. 12. Blast lamp.

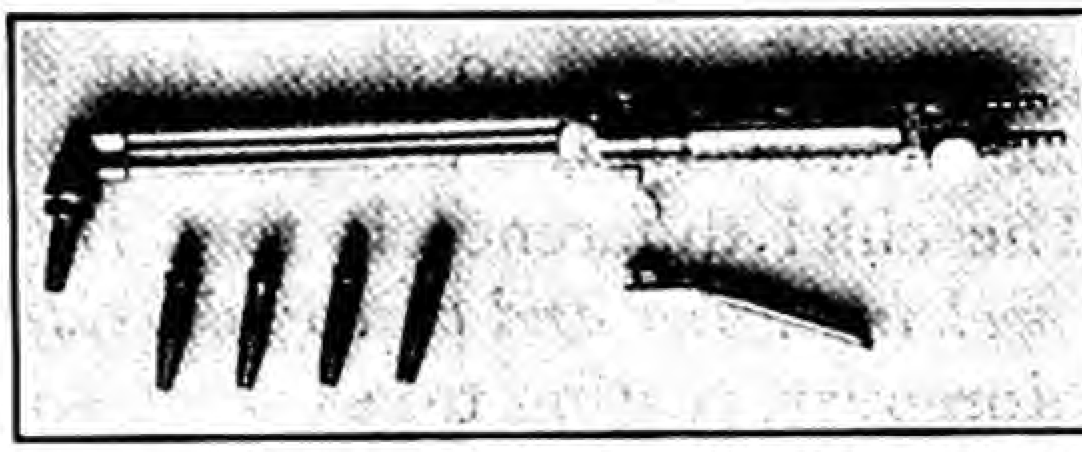
3. *The blast lamp* (Fig. 12). *Compressed air* is forced into the center of the flame, hence almost enough oxygen is present for complete combustion, *in the innermost zone of flame.* The volume of the flame is consequently less than would be obtained with a Bunsen burner, with the same rate of flow of gas. The same amount of heat is liberated, but within a very small volume, hence the temperature rises very high.

4. *The cutting or welding torch* (Fig. 13). Hydrogen or acetylene, C_2H_2, is mixed with *pure oxygen*, at the tip of the torch. Since the nitrogen of the air is then absent, the molecules of the fuel gas encounter and combine with molecules of oxygen even

more quickly than in a blast lamp. The flame, for a given rate of gas flow, is therefore limited to a still smaller volume. For this reason, and because no heat is wasted in raising the temperature of nitrogen, the flame is very hot. (Ex. 12, 13.)

The oxyhydrogen flame attains a temperature of about 2800°C, and the oxy-acetylene flame one of about 3300°C.

5. *Spontaneous combustion.* Piles of slack coal, coal dust about mines, dry peat bogs, heaps of fermenting straw or tanbark, and piles of oily rags or waste often catch fire of themselves. Such fires always start in material subject to oxidation or decay —processes that slowly release heat, even at room temperatures. Furthermore, such material is a poor conductor of heat. Heat that is released within the mass by the slow oxidation is *retained*. The temperature mounts higher and higher, combustible gases begin to be expelled, and at last the mass bursts into flame. This is **spontaneous combustion.**



Courtesy of the Air Reduction Sales Co.

FIG. 13. Oxyacetylene cutting torch.

To avoid fire risk, avoid accumulating readily oxidizable material in very large piles, and so give the heat liberated a better chance to be dissipated.

Demonstration: The interior of a wad of slightly moist straw, compressed into a beaker and left standing for a week, is well above room temperature.

6. *Kindling temperature.* Demonstration: **Kindling temperature** is determined by nature of substance, fineness of subdivision, opportunity for loss of heat (for example, by being conducted away through a metal, or by being used in evaporating water).

Demonstration of a dust explosion (§ 56, item 3).

7. *Putting out fires.* Water puts out a fire not only (1) because its temperature is low but also (2) because it takes heat to evaporate water, and this must be supplied by the fire. The water vapor, moreover, (3) drives back the air and prevents oxygen from reaching the burning material so easily.

Fire extinguishers usually blanket the flame to be extinguished with carbon dioxide gas or the vapors of some incombustible liquid, or with bubbles filled with carbon dioxide. They thus diminish the supply of oxygen.

Demonstration: Fire-foam and Pyrene.

53. Oxidation and Reduction

The most important chemical property of oxygen is its ability to combine directly with most other elements, including both metals and non-metals, to form compounds called *oxides*.

Reactions in which different substances combine directly with oxygen are examples of *oxidation*. The term was long ago extended to include *all reactions in which something combines directly with oxygen, or with any other non-metal*, such as chlorine or sulfur. This seems logical, since many metals burn vigorously in chlorine or in sulfur vapor, emitting heat and light, just as they do in oxygen.

The reverse process, in which a substance is made to part with its oxygen, is termed *reduction*. This word was also long ago extended to *all reactions in which oxygen or any other non-metal* is withdrawn from combination with a metal.[1]

54. Other Processes Involving Union with Oxygen

1. *Rusting*. When moist iron filings rust in a confined space over water, it is easy to show that some of the air disappears. The iron combines with the oxygen of the air, just as iron does when it burns. The chief difference is that *rusting is accompanied by other changes, involving water and carbon dioxide, hence iron rust is not pure iron oxide.* Moreover, rusting takes place so slowly and the heat that is evolved is liberated so slowly that the temperature of the metal does not rise appreciably.

2. *Respiration* (breathing). Respiration was shown by Lavoisier to resemble combustion in that it consists of the direct union of oxygen with other materials. A part of the oxygen in the air drawn into the lungs combines with the red corpuscles of the blood, and is carried by them to all parts of the body.

In all parts of the body, then, slow oxidation takes place, in which chemical substances derived from the food are combined with oxygen, in a number of successive stages, ultimately to form carbon dioxide, water, and other products. This process supplies energy for muscular movements and other activities of life, and liberates heat to keep the body warm. The carbon dioxide thus produced is exhaled from the lungs. The exhaled air may contain so little oxygen and so much carbon dioxide that it will extinguish a candle. (Ex. 14.)

A candle goes out when the oxygen in the air is diminished from the usual 21 per cent to about 17 per cent. Human life is still sustained at a somewhat lower figure if other conditions are right; and certain *bacteria* (the so-called anaerobic bacteria) actually thrive best in the nearly complete absence of oxygen.

3. *Decay*. When wood decays, molds and bacteria penetrate it and cause it gradually to combine with the oxygen of the air to form carbon dioxide and water. A decaying log in a forest is at length as completely and as truly burned as if consumed in a furnace. The quantity of heat released is the same in both processes, though this heat makes itself more evident when the log is burned in the furnace because it is released quickly, in a confined space. (Ex. 15.)

[1] In recent years oxidation and reduction have been given still broader meanings to be discussed in a later chapter (§ 255).

55. Distinction between Metals and Non-Metals

About 70 of the ninety-odd known elements are *metals*. The others, about 20 in number, are classed as *non-metals*, including six inert gases.

Most metals may readily be recognized (1) by their mirror-like surface or *metallic luster*, when polished, and (2) by their being *good conductors of heat and electricity*. Many metals (conspicuously gold and silver) are (3) very *malleable* (can be rolled or beaten into sheets) and (4) very *ductile* (can be drawn into wire).

Non-metals, by contrast, are either *gases* at ordinary temperatures or *brittle solids*, with at most a *vitreous* (glassy) *luster* (though bromine is a heavy, red-brown *liquid*).

The preceding physical properties, by which metals are distinguished from non-metals, are not very prominently displayed by certain elements, such as antimony and tellurium, which lie on the borderline between the two classes. These are often called *semi-metals*.

Metals may often be distinguished from non-metals by a simple chemical test:

1. Burn the element in air or oxygen, thus forming an oxide.
2. Place the oxide in water (if necessary, *boil* it with water). If it dissolves in (and combines with) the water to form a solution having an *alkaline reaction* (namely, turning red litmus *blue*), the element tested is a metal. If the oxide reacts with water to form a solution having an *acid reaction* (turning blue litmus *red*) the element tested is a non-metal.

To summarize:

$$\text{Certain metals} \xrightarrow{+\text{ Oxygen}} \text{Metallic oxides} \xrightarrow{+\text{ Water}} \text{Alkalies (§ 192)}$$

$$\text{Certain non-metals} \xrightarrow{+\text{ Oxygen}} \text{Non-metallic oxides} \xrightarrow{+\text{ Water}} \text{Acids (§ 164)}$$

The test just described cannot be applied to a few elements (the inert gases and chlorine) which fail to combine directly with oxygen.

It also cannot be applied to most of the heavy metals such as iron, tin, and copper (middle part of the periodic table, § 215) or to several non-metals, because their oxides fail to react with water to give soluble products (thus making impossible a test with litmus). Silicon, for example, burns to form silicon dioxide or ordinary sand, and iron burns to form magnetic iron oxide; both these substances are practically completely insoluble in water, hence a test with litmus is impossible. (Ex. 16.)

56. What Determines Rate of Combustion?

The rate at which a material burns depends on several factors:

1. *The nature of the substance.* Other things being equal, iron oxidizes more readily than mercury or silver.

2. *The temperature.* The higher the temperature of a piece of charcoal, the faster it will burn. Iron rusts more quickly in hot water than in cold, if the water is equally aerated.

Even a small increase of temperature sometimes has a great effect: Respiration strikes up a swifter pace with warm-blooded animals; and decay, in tropical climates, is amazingly rapid.

Moist material burns with difficulty because it takes heat to evaporate the water that it contains, and the temperature is therefore lowered. Too vigorous fanning of a fire may lower its temperature and put it out, whereas gentle fanning helps bring it oxygen.

3. *The surface exposed.* The more surface the material being burned presents to the air, the more rapidly burning takes place. That is why we whittle a stick into shavings to start a fire. The finer the shavings, the better the fire takes hold. Charred cotton or linen fibers —used in the old-fashioned tinderboxes—would be better yet.

A photographer's photoflash bulb flashes up and dies away within perhaps a twentieth of a second, because the aluminum foil or fiber that it contains presents an enormous surface, burns in pure oxygen, and liberates so much heat when it starts burning that it is immediately raised to a very high temperature.

When combustible material is very finely divided it may hover in the air as *flammable dust.* A tremendous surface, for a given weight of material, is then exposed to the action of the oxygen. Each particle is surrounded by a plentiful supply of oxygen. This is the best possible condition for rapid combustion. Any chance spark may set the mixture off—a *dust explosion.* Coal mines, factories and grain elevators, in absence of dust-removing equipment, have been completely wrecked by such explosions. Housewives have been killed by throwing combustible dust into an incinerator. (Ex. 17.)

4. *The concentration of the oxygen* (the amount present in unit volume). There is about five times as much oxygen in a given volume of pure oxygen as in the same volume of air. Thus union with oxygen goes on about five times as fast in pure oxygen as in air, other things being equal.

57. Direct Union of Oxygen with Oxides

Not only elements but also many compounds, including some that already contain oxygen, may be made to combine directly with oxygen.

The following are examples of oxides which by union with a further quantity of oxygen may be raised to a "higher stage of oxidation":

NO	+	O_2	→	NO_2	(unbalanced)
Nitric oxide (colorless gas)				Nitrogen dioxide (brown gas)	
CO	+	O_2	→	CO_2	(unbalanced)
Carbon monoxide (Colorless gas, very poisonous)				Carbon dioxide (colorless gas)	
SO_2	+	O_2	→	SO_3	(unbalanced)
Sulfur dioxide (colorless gas)				Sulfur trioxide (colorless liquid) or white solid)	
P_2O_3	+	O_2	→	P_2O_5	
Phosphorus trioxide (white solid)				Phosphorus pentoxide (white solid)	
Cu_2O	+	O_2	→	CuO	(unbalanced)
Cuprous oxide (brick-red solid)				Cupric oxide (black solid)	
FeO	+	O_2	→	Fe_2O_3	(unbalanced)
Ferrous oxide (white solid)				Ferric oxide (brown solid)	

Since these are all important substances, the student should remember their names and formulas. These formulations will also give further exercise in balancing. (Ex. 18.)

58. The Law of Multiple Proportions

Experiments have shown that the weights of oxygen combined with any given weight of carbon, in the two chief oxides of carbon, are in the ratio 1:2. Weights of oxygen combined with any given weight of sulfur, in the two chief oxides of sulfur, are in the ratio of 2:3. Weights of oxygen combined with any given weight of phosphorus, in the two chief oxides of phosphorus, are in the ratio of 3:5. Observe how constantly we encounter *ratios of small whole numbers!*

Summarizing: *There is a ratio of small whole numbers between the different weights of any one element that combine with a chosen weight of any other, to form a series of related compounds.* This is the *Law of Multiple Proportions* or *Related Composition.* Note that it compares different weights *of the same element,* as they appear in different compounds, in combination with a chosen weight of any other element.

This law was suggested by experiments made before the work of Dalton. His atomic theory merely furnished a simple explanation. The different weights of an element that combine with a chosen weight

of any other must be in the ratio of small whole numbers, since only small whole numbers of atoms combine, in forming molecules. View this law, therefore, as an obvious consequence of the Atomic Theory, not as something to be separately memorized. (Ex. 19, 20.)

59. What Is Formed When Fuels Burn?

Gaseous fuels are usually mixtures of *hydrocarbons* (substances containing only the elements carbon and hydrogen, in chemical union); but some of them contain carbon monoxide, CO. Liquid fuels, such as fuel oil and gasoline, are also hydrocarbons. The most important solid fuels, wood and coal, are mixtures of a great many complex substances, chiefly composed of carbon, hydrogen, and oxygen.

When a fuel is burned, the carbon in it is converted into carbon monoxide or carbon dioxide, according as the supply of oxygen is limited or plentiful:

$$C + \underset{\substack{\text{(In}\\ \text{limited}\\ \text{supply)}}}{O_2} \rightarrow \underset{\substack{\text{Carbon monoxide}\\ \text{(colorless gas,}\\ \text{poisonous)}}}{CO} \text{ (unbalanced)}$$

$$C + \underset{\substack{\text{(In}\\ \text{plentiful}\\ \text{supply)}}}{O_2} \rightarrow \underset{\substack{\text{Carbon}\\ \text{dioxide}\\ \text{(colorless gas)}}}{CO_2}$$

When all the carbon in a fuel is oxidized to carbon dioxide and all the hydrogen to water, we say that we have *complete combustion*. It is important to have complete combustion, whenever possible, in burning fuels, since much more heat is then liberated than would occur if the carbon burned to produce carbon monoxide.

Since a fuel is nearly always a complex mixture, no one chemical equation will represent its combustion exactly; but if we represent gasoline by one of its chief components, heptane, C_7H_{16}, an approximate formulation would be

$$C_7H_{16} + O_2 \rightarrow CO_2 + H_2O \text{ (unbalanced)}$$

Actually, in an automotive engine, a large part of the carbon in the gasoline is oxidized to carbon monoxide rather than carbon dioxide. This may seem surprising, since plenty of air is used. The explanation is that carbon dioxide, at the high temperatures attained in an automotive engine, is partially *dissociated* (reversibly decomposed):

$$2CO_2 \rightleftharpoons 2CO + O_2$$

Note the use of reversed arrows, $\rightleftharpoons$, to indicate a reaction that is reversible.

Balance the preceding formulations. (Ex. 21, 22.)

60. Burning a Solid Fuel in a Stove or Furnace

In a stove or furnace (Fig. 14), we can usually distinguish three separate zones of combustion:

1. Carbon, at the bottom of the mass of solid fuel, gets a plentiful supply of air through the grates, and so burns directly to carbon dioxide.

2. Carbon dioxide, in rising through the overlying bed of glowing coals (chiefly red-hot carbon), combines with carbon to form carbon monoxide.

$$CO_2 + C \rightarrow 2CO$$

3. Finally, at the top of the bed of fuel, in air admitted through openings in the furnace doors, carbon monoxide burns to form carbon dioxide.

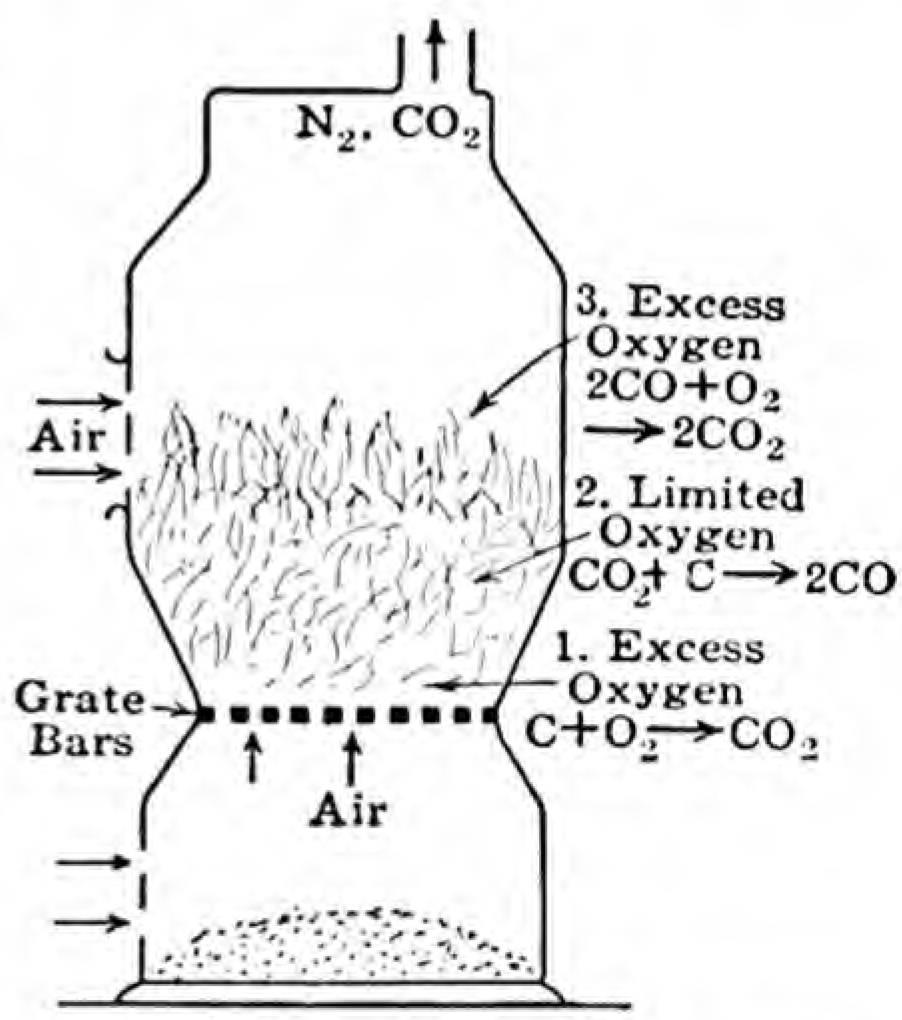


FIG. 14. Zones of combustion.

When the furnace is first charged, a luminous or smoky flame is produced, from burning hydrocarbons expelled from the coal or wood by the heat. Later, bluish flames may be seen, playing over the surface of red-hot coals. These are burning carbon monoxide.

61. Fire-Resistant and Fire-Proof Materials

Certain metals (gold, platinum, silver) fail to combine with oxygen directly, though they will melt at very high temperatures. Other metals (iron, steel, nickel, copper) melt only at temperatures above those reached in ordinary fires, and burn at such temperatures only if they are so divided as to expose relatively great surface, thus favoring oxidation.

Bricks, terra-cotta, many kinds of building stone, asbestos, quartz, and similar materials are fire-resistant because (1) they are not readily melted or decomposed by heat and (2) they are composed of substances that are already fully oxidized. Most of them, in fact, are more than one-third oxygen, so firmly combined with silicon and other elements that even the highest temperatures fail to disengage it.

The most conspicuously fire-resistant of such fully oxidized materials are called *refractories*. Examples are fire-clay, aluminum oxide, and quicklime. The best of them will withstand temperatures at which iron and steel melt to liquid, and lead and zinc vaporize.

Wood is made fire-resistant by being impregnated with incombustible chemical substances, such as a mixture of *alum* and *ammonium phosphate*. This calls for treatment of the wood with solutions of these salts, in closed chambers, under pressure, with slow drying afterward, lasting several weeks. The action of a flame on such wood is merely to char it. Ammonia vapors are expelled and tend to displace the air, and so extinguish the flame. Meanwhile, the alum coats the charred material with a fire-resistant glaze. Fabrics are often made fire-resistant by being dipped into a solution of ammonium sulfamate.

62. Uses of Oxygen

Gaseous oxygen is sold in strong steel cylinders, in which it is retained under high pressures, up to about 150 atmospheres. Under such conditions it is nevertheless still in the gaseous form. *Liquid oxygen* may be shipped in vacuum-jacketed metallic containers, commonly holding up to about 25 gallons. Such containers cannot be closely stoppered, else the pressure set up by the evaporating gas would burst them; but the loss by evaporation hardly exceeds 5 per cent a day.

Oxygen is used:

1. In medical practice, for the relief of impeded respiration (for example, in pneumonia), and in the treatment of cases of poisoning by nitric acid fumes or vapors of aniline or nitrobenzene. Such poisoning is somewhat frequent among workmen engaged in manufacturing explosives.

2. In producing anesthesia with nitrous oxide or ethylene, oxygen is usually administered as well.

3. In welding and cutting iron and steel by the oxyacetylene torch. Pieces up to about half an inch in thickness are now commonly welded by this method, which is gradually displacing riveting in the erection of steel frameworks of buildings, bridges, and even ships. Heavy pieces and certain alloy steels are commonly welded with the electric arc rather than by oxyacetylene.

In tearing down the steel frameworks of damaged or obsolete buildings, in cutting holes in steel plates, and for similar purposes, the oxyacetylene torch has become indispensable. Steel many inches thick may be sliced through like cheese. The metal is raised to incandescence by the torch, then an excess of oxygen is turned on and the metal is

burned away. A special form of the oxyacetylene torch will even cut steel under water, but it is customary to heat the submerged metal to incandescence with an electric arc, then burn it away in a stream of oxygen.

4. Oxygen is used in connection with hydrogen in oxyhydrogen welding (§ 95).

5. Cartridges of carbon dust, wet with liquid oxygen, have been used as a substitute for dynamite in coal mining. They have the advantage that their explosion does not produce poisonous fumes, but the disadvantage of being readily set off prematurely, by electric sparks. (Ex. 23, 24.)

6. An important recent application of oxygen is in removing Fe_3O_4 scale from sheet steel as it issues from the sheet rolls. Jets of oxygen, playing of the surface of the white hot steel, oxidize some of it to Fe_3O_4; but the oxidation liberates so much heat that the scale melts and is blown away, leaving the surface of the metal clean.

63. Ozone

Ozone is a form of oxygen of extraordinary chemical activity. Thus metallic silver, which remains bright for years in ordinary oxygen, becomes covered with a brown film of an oxide of silver when exposed to air containing a trace of ozone.

The peculiar pungent odor of ozone is often noticed in thunder storms and around wireless transmission sets or other high-tension elec-

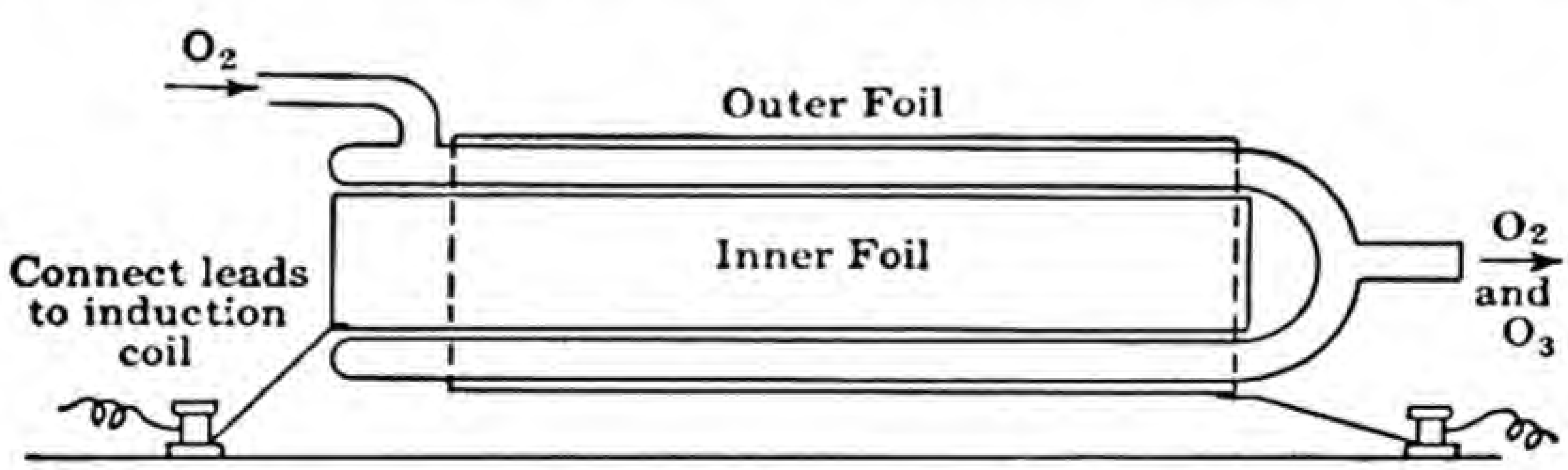


FIG. 15. Laboratory preparation of ozone.

trical apparatus. It is formed in nature whenever a lightning discharge passes through the air, and is constantly produced in the upper regions of the atmosphere by the action of the ultraviolet light of the sun's rays on ordinary oxygen.

In the laboratory, dry air may most easily be ozonized by passing it between two plates, charged with electricity (several thousand volts) from a source of alternating current (Fig. 15). The *silent electrical discharge* that takes place between the plates is usually accompanied by a

pale bluish light, rich in ultraviolet rays, and the air leaving the apparatus is found to contain 1 per cent or so of ozone. (Actual *sparks* do not pass between the two plates.)

Oxygen containing ozone is somewhat denser than ordinary oxygen. This is an indication that its molecules are heavier, since equal volumes of pure oxygen and pure ozone contain very nearly the same number of molecules (§ 31). Pure ozone can readily be obtained by cooling ozonized air to about $-180°C$. The ozone separates as a deep blue liquid, whose vapors have a density approaching that indicated by the formula O_3.

When ozone oxidizes readily oxidizable substances only a third of its oxygen takes part in the reaction, in other words, only one of the three atoms of oxygen in each molecule.

The formation of ozone from ordinary oxygen is a reversible reaction:

$$3O_2 \underset{\text{Decomposition of ozone}}{\overset{\text{Formation of ozone}}{\rightleftarrows}} 2O_3$$

That is why the conversion of oxygen into ozone, by a silent electric discharge, is never complete. After a time the discharge produces ozone at the same rate that ozone is being decomposed—a case of *chemical equilibrium*. (Ex. 25, 26.)

Small amounts of ozone in the atmosphere are best detected by the fact that it produces a deep-blue color in paper that has been dipped in a solution containing *starch* and *potassium iodide*. This test is not an entirely conclusive one, for chlorine and a number of other substances, classed as *oxidizing agents*, produce the same result.

Ozonized air has sometimes been used as a disinfectant or for sterilizing drinking water. It has the advantage of leaving behind no other product than oxygen, after it has done its work.

(Review questions, Ex. 27–30.)

64. Retrospect and Anticipation

We have seen that the atomic-molecular theory, in the form given it by Dalton, explains chemical transformations as being accomplished by rearranging or recombining atoms within molecules. Better yet, it enables us to determine what kinds of atoms and how many of each kind are contained in any given kind of molecule. With the aid of chemical formulas, thus derived, the proportions by weight in which chemical substances interact are made predictable. Thus we account for the Law of Conservation of Matter, the Law of Definite Propor-

tions, and the Law of Multiple Proportions, which otherwise would have remained mysteries, however well established as experimental results.

The chapter just completed has presented *combustion*, *respiration*, *rusting*, and *decay* as processes in which molecules of the substances being oxidized combine with those of oxygen to form molecules of carbon dioxide, water, and other products. It then adds details to explain, for example, why combustion is sometimes rapid and sometimes slow, and why a hotter flame is obtained in burning a gaseous fuel in certain types of burners or in pure oxygen.

In explaining all this we have, nevertheless, met with new facts that raise new questions:

Why should atoms combine at all in forming molecules? What force holds them together?

Why should specified kinds of atoms often combine in different ways or in more than one porportion, to form a number of different compounds (§ 58)?

Why are some compounds easy and others hard or impossible to decompose by heating?

What is heat, why is it released in many or most chemical reactions, and why do certain reactions release more heat than others?

Why is carbon, a solid, converted into a gas, by direct union with oxygen?

Why does oxygen, compressed into cylinders for industrial use, nevertheless remain gaseous, whereas ammonia and many other gases condense to liquids?

Why are certain substances gases, others liquids, and still others solids, all at the same temperature?

When water is electrolyzed, why do the two products appear in separate places, in spite of the fact that they must both be present in every molecule of water that is decomposed?

Why does the addition of an acid or an alkali render water a better conductor of electricity?

What is the nature of an electric current, and what actually happens at the electrodes as the products of the electrolysis are there set free?

Just how does a catalyst speed up or retard a reaction?

It begins to look as if the incident really happened in which someone remarked, "I knew all about that subject until you began to ask me questions." Our purpose is to rouse the reader to ask himself questions. If he begins to inquire *why* at every turn he will be on his way to learn what is meant by chemical thinking. Many of the ques-

tions just asked will be answered in later chapters. For others, no one yet knows the answer. That is why chemical research is still carried on, in thousands of laboratories, all over the world.

TECHNICAL WORDS

Elementary—in the form of an element, uncombined with others.

Catalyzer or **catalyst,** p. 47.

Catalysis—the action of a catalyst in altering the rate at which a chemical reaction takes place.

Reaction summary—a brief indication of the names of the reactants entering into a reaction and the resultants produced by it.

Oxide—a compound formed by direct union of oxygen with some other element.

Metallic oxide, non-metallic oxide—oxide formed from a metal or non-metal, respectively.

Peroxide—an oxide that is capable of reacting with water or acids to form hydrogen peroxide, H_2O_2. Examples: Na_2O_2, BaO_2; but CO_2, NO_2, SO_3, PbO_2 are not classed as peroxides.

Electrolysis—decomposing a substance by passing an electric current through it, or through a solution containing it.

Electrode, p. 48. **Anode, cathode,** p. 48. **Incandescent,** p. 52.

Formulation—a method of representing chemical reactions, in which chemical formulas are used to indicate the *identity* of the reactants and resultants, without any attempt to indicate *relative numbers of molecules or relative weights.*

Chemical equation—a method of representing chemical reactions, using proper multiples of chemical formulas to indicate relative numbers of molecules, and hence the *relative weights* of the reactants and resultants.

Oxidation, reduction (preliminary definitions), pp. 53, 54.

Oxidizing agent or **oxidant**—a substance capable of oxidizing another.

Combustion, p. 52. **Flame,** p. 52. **Complete combustion,** p. 58.

Microorganism—any organism (plant or animal) of microscopic size.

Bacteria (sing., **bacterium**)—one-celled vegetable microorganisms.

Molds—a group of microorganisms, devoid of chlorophyll; normally many-celled and spore-producing.

Decay, putrefaction—processes in which complicated products, produced by living plants and animals, are broken down and oxidized to form simpler products, by the action of microorganisms. In *decay*, there is a plentiful supply of air, oxidation is nearly complete, and the final products include carbon dioxide, water, and ammonia or ammonium salts; in *putrefaction*, the supply of air is limited, and complex organic compounds of unpleasant odor are produced.

Spontaneous combustion—burning that is self-initiated.

Kindling temperature—the temperature at which a material catches fire and continues to burn, after the original source of heat has been withdrawn (p. 53).

Malleable, ductile, p. 55.

Alkaline reaction—turning red litmus blue, or producing a corresponding color change with some other indicator. **Acid reaction,** left for student to define.

Metals, non-metals, p. 55. **Metallic luster, vitreous luster,** p. 55.

Flammable—capable of being set on fire. This word is tending to supersede *inflammable*, which is likely to be confused with its opposite, non-flammable.

Concentration—weight or number of particles (molecules or ions) in unit volume. The term is usually applied to some component of a mixture, whereas *density* (p. 13) refers to *total* weight in unit volume, for the material or mixture as a whole.

Hydrocarbon, p. 58.

Refractories—materials that do not burn and that melt only at very high temperatures.

Equilibrium—a condition of balance between two opposing forces or processes.

Chemical equilibrium—a condition of balance between two chemical reactions, proceeding at equal rates, each undoing the work of the other. Each of the opposing reactions therefore remains incomplete, no matter how long the reacting substances are left in contact.

Ozone—triatomic oxygen—in other words, oxygen containing three atoms in each molecule.

Disinfectant, antiseptic—capable, respectively, of *ending* or *preventing* infection by microorganisms. (Note the distinction.) To "sterilize" a material is to destroy microorganisms or their spores.

Summary

Most important items in this chapter: Several ways to prepare oxygen (§ 45). How an equation is balanced (§§ 46, 47). How an equation is made to show relative weights (§§ 49, 50). Meaning of oxidation and reduction (§ 53). Zones of combustion, within a flame or furnace (§§ 52, 60). Rate of combustion (§ 56). Test to distinguish metals from non-metals (§ 55). Uses of oxygen (§ 62).

§ 43. Where oxygen is chiefly found, combined and uncombined.

§ 44. Whether air is a chemical compound or a mere mixture. How oxygen is prepared from air and from water. Chief source of oxygen for industrial uses.

§ 45. How oxygen is prepared from potassium chlorate. Means used to increase the rate of liberation of oxygen. Name of the solid residue remaining after the oxygen has escaped.

Another substance that liberates oxygen on being heated, with the name and formula of the solid residue.

How oxygen may be prepared from sodium peroxide; an unbalanced formulation to represent this reaction.

Sketch of the apparatus in which water is decomposed as a lecture experiment; reason for adding a little acid or alkali to the water; which gas is obtained at the positively charged electrode, and which at the negatively charged electrode. Relative volumes of the two gases. Names given to the two electrodes.

§§ 46, 47. Distinction between a formulation and a chemical reaction.

§ 48. What one should and should not attempt to memorize about important chemical reactions.

§§ 49, 50. Three meanings for every balanced chemical equation.

§ 51. What we mean by physical properties. Five physical properties usually listed in describing gases. A rough statement of these properties for oxygen.

§ 52. What we mean by combustion, as distinguished from oxidation in general. The nature of flame.

The three zones of a Bunsen flame. Which part of a flame has a reducing action and which an oxidizing action.

A brief description of the blast lamp and welding torch, explaining why a higher temperature is obtained in each than would be obtained with a Bunsen burner.

What materials are subject to spontaneous combustion. How the danger may be lessened.

What circumstances determine the kindling temperature of a material.

Two ways in which a fire extinguisher usually acts.

§ 53. The earliest meaning and a later meaning of the terms oxidation and reduction.

§ 54. One respect in which rusting is like combustion, and two respects in which it is different.

What happens in respiration.

What happens in decay. Why the heat released in decay is ordinarily not evident.

§ 55. Some physical properties by which metals may often be distinguished from non-metals.

Two steps in a chemical test by which metals may sometimes be distinguished from non-metals.

Two reasons why this test often cannot be applied.

§ 56. Four factors that determine rate of combustion.

§ 57. The names and formulas of several oxides that can be made to combine with a further quantity of oxygen. The names and formulas of the products obtained.

§ 58. A statement of the Law of Multiple Proportions or Related Composition. (Be able to cite one of the three examples given.)

§ 59. What becomes of the carbon when a fuel is burned in a *limited* or in a *plentiful* supply of air.

What becomes of the hydrogen contained in a fuel, when the fuel is burned.

§ 60. Three separate zones of combustion, within a stove or a furnace, with an equation to represent what takes place in each.

§ 61. Two reasons why materials may be fire-resistant.

How wood may be made fire-resistant, and what materials are commonly used for this purpose.

§ 62. How gaseous oxygen and liquid oxygen respectively are transported in commerce.

Two separate uses for oxygen in medicine, and at least two important industrial uses.

§ 63. What ozone is, how it is made, and how it is detected.

An equation to represent the reversible formation of ozone from ordinary oxygen.

Exercises

In solving the problems in this book round off atomic weights to the nearest unit, except Cl = 35.5, Cu = 63.5, Hg = 200.5.

1. Write and balance an equation for the electrolysis of water, recalling that hydrogen and oxygen gases must be represented by H_2 and O_2, respectively.

2. Write and balance an equation for the reaction of ferric oxide, Fe_2O_3, with hydrogen gas, the products being metallic iron and water vapor.

3. Write and balance an equation for the decomposition of potassium nitrate, KNO_3, by heating, the products being potassium nitrite, KNO_2, and oxygen gas.

4. When 24.5 grams of potassium chlorate is heated, what weight of potassium chloride and what weight of oxygen gas are obtained? 149, 960

5. To obtain 16 grams of oxygen, what weight of potassium chlorate must be decomposed? 408

6. If 14.9 grams of potassium chloride is obtained by heating potassium chlorate, what weight of the latter was taken and what weight of oxygen obtained? 245, 960

7. Calculate percentage of potassium in potassium perchlorate, $KClO_4$. 282

8. Which contains the higher percentage of oxygen, potassium chlorate or sodium chlorate, $NaClO_3$?

9. In the preparation of oxygen from sodium peroxide, what weight of water must be used for every 156 parts by weight of sodium peroxide? 360

Roughly what fraction is this of the weight of sodium peroxide?

Then about what weight of water will be needed to decompose 50 grams of sodium peroxide?

10. Write and balance equations for the preparation of oxygen gas, O_2, from mercuric oxide, HgO, the other product being metallic mercury. What weight of mercuric oxide must be decomposed to yield 32 grams of oxygen? 433

11. Write and balance an equation for the preparation of oxygen gas, O_2, by heating manganese dioxide, MnO_2, to very high temperatures, the product being mangano-manganic oxide, Mn_3O_4. Underneath each of the three formulas appearing in the balanced equation, set down the number of weight units that the equation indicates.

12. Write an equation for burning acetylene in the inner zone of an oxyacetylene flame. The products are carbon monoxide and hydrogen.

Write equations for the further combustion of these two products in the outer zone of the flame.

13. If the oxygen produced in the electrolysis of water weighs 8 times as much as the hydrogen, but occupies only half the volume of the hydrogen, how does the density (p. 13) of the oxygen compare with that of hydrogen?

14. In view of respiration of living seeds, and respiration as a slow combustion, what do you think of the claim that seeds found in Egyptian tombs have germinated after 4000 years?

15. Wood that is merely moist is likely to decay rapidly. If it is buried in mud at the bottom of a lake or river, it may be preserved for centuries. Explain.

16. Selenium is a non-metal. Tell how you would attempt to prove this in the laboratory, what result you would expect to get in the test made, and what might cause the test to be inconclusive.

17. Rock powder is frequently scattered over coal-dust-covered surfaces in coal mines as a protection against dust explosions. Explain how it acts.

18. Balance formulations for the reactions in § 57, and indicate in each case how many molecules of oxygen are needed and how many molecules of each resultant are produced.

19. A certain calcium compound contains 40 parts by weight of calcium, combined with 12 parts by weight of carbon, and some oxygen. Another contains $1\frac{2}{3}$ parts by weight of calcium for 1 part by weight of carbon. Express these results in such a way that we shall have *the same weight of carbon in the two compounds;* then show that the two different weights of calcium are simply related to each other.

20. From the formula of the two oxides of copper, Cu_2O and CuO, calculate what weight of copper in each oxide combines with 1 gram of oxygen. Show that the results illustrate the Law of Multiple Proportions. 400, 800

21. Balance equations for the reactions in §57.

22. Write a balanced equation for the preparation of oxygen from barium per-

oxide, BaO_2, the other product being barium oxide, BaO. Emphasize this as a reversible reaction.

23. How could it be proved that ordinary commercial oxygen actually contains a small percentage of a chemically inert gas?

24. When a substance is burned under a bell-jar over water (Fig. 10) why does the volume of the air within the bell-jar at first increase a little, then gradually decrease?

25. If 90 liters (volume) of oxygen could be completely converted into ozone, what volume would it occupy? (*Suggestion:* three molecules of oxygen produce two molecules of ozone, hence three volumes produce two volumes, by Avogadro's Principle.) 600

26. If 10 liters of pure ozone were decomposed, what volume of ordinary oxygen would be produced? 150

27. Write an equation for the formation of "hammer scale," Fe_3O_4, on iron which is heated in contact with air.

28. What do we mean by saying that a material is incandescent? A luminous gas flame may be rendered much less luminous by lowering over it a heavy coil of copper wire. Explain.

29. Smoke is unburned carbon. Explain why a candle wick that protrudes through the top of the flame will usually smoke.

30. Write the equations for the complete combustion of the following fuel gases: acetylene, C_2H_2; ethane, C_2H_6; propane, C_3H_8.

Chapter 6

ENERGY

65. Energy Changes in Chemical Reactions

The transformations of matter which are the chief concern of chemistry are always accompanied by transformations of *energy*. There are indeed some reactions, for example those in burning fuels, in which we are chiefly concerned with the energy that the reaction yields. Its material products (water vapor, carbon dioxide, and ashes) we discard, without giving them a thought.

Matter and energy are such fundamental concepts that they come close to being undefinable. Perhaps the best we can do is say that *matter is anything which has mass* (defined on p. 28). Do not trivially define matter as anything that occupies space. Ability to occupy space is merely incidental, and varies with the temperature of a body and with the pressure upon it; whereas its mass remains unaltered, in spite of the alteration in weight which would occur if the body were transported to the moon.

Energy is anything that can do work (in other words, anything that can set a body in motion or maintain it in motion in spite of the opposition of a *force* (a push or a pull). Since all other forms of energy tend to take the form of heat and can be *completely* converted into heat, it is also satisfactory to say that *energy is heat, or anything that can be converted into heat.*

We have already learned that energy is set free (usually as heat energy) during reactions of oxidation, including combustion, respiration, and even decay. There are a few reactions, however, which can only be accomplished if some outside source supplies energy, commonly as heat (when carbon dioxide reacts with heated carbon to produce carbon monoxide, § 60) or as electrical energy—when water is decomposed by the passage of an electric current (§ 45, item 5).

66. Kinds of Energy

There are three fundamental kinds of energy:

1. *Radiant energy is energy in the form of visible or invisible light.* (The latter is a colloquial term which includes infrared and ultraviolet

light, X-rays, and sometimes even radio waves.) Radiant energy is transmitted in *straight lines* through homogeneous matter or through empty space. In empty space it seems always to have the same velocity, regardless of its character.

This *free space velocity of radiant energy* (commonly referred to as the "speed of light") is about 186,000 miles a second (or, almost precisely, 3×10^{10} centimeters per second). (Refer to Appendix E for a discussion of the use of powers of ten to express very large or very small numbers.) Through material bodies, radiant energy moves with a somewhat smaller velocity, which may be found by dividing the velocity in a vacuum by the *index of refraction* of the material.

2. *Kinetic energy is energy of motion.* All moving bodies possess kinetic energy in proportion to their *mass* and their *velocity squared.* That the kinetic energy of a moving automobile (namely, its capacity for doing work or doing damage) is actually proportional to the square of its velocity is known to every driver who is sober. Doubling the velocity doubles the time that is needed to bring the car to a stop, after applying a given force by the brakes; but during this doubled time the car will be traveling twice as fast, hence will traverse 4 times the former distance and so will do 4 times as much work.

In the metric system, kinetic energy is given by the formula

$$\underset{\text{(ergs)}}{K.E.} = \tfrac{1}{2} \times \underset{\text{(grams)}}{Mass} \times \underset{\text{(centimeters per second)}^2}{Velocity\ squared}$$

Observe the units in which these three quantities are expressed. The $\frac{1}{2}$ is a consequence of the manner in which an erg is defined, relative to the *fundamental metric units* (the centimeter, gram, and second). (Ex. 1, 2.)

3. *Potential energy is energy due to the attractive and repulsive forces between the bodies that compose a group or system of bodies.* A book on a table (more properly, the *system* book + earth) possesses potential energy because of the force of gravitational attraction between book and the earth. Two heavy balls, suspended by steel wires and brought near each other, also possess potential energy because of their gravitational attraction for each other. This is very slight, but it is distinctly measurable, since it causes the two suspension wires, otherwise vertical, to converge slightly.

Do not trivially define potential energy as energy of *position.* It is true that an object has more potential energy when on a table than it has when it has fallen to a lower position (on the floor); and in

general *the potential energy of any system of bodies will vary with their relative positions.* But the essential thing is the *attractive or repulsive forces* without which the system would possess no potential energy, whatever the positions of its component parts.

Many other kinds of energy have been recognized, but they are all really based upon and resolvable into the three sorts just mentioned. When we speak of the *magnetic energy* of a bar magnet, the *surface energy* of a soap bubble, the *torsional energy* of a coiled spring, the *chemical energy* of a fuel, the *electrical energy* of a current in a wire, or the *heat energy* released in combustion, we are merely giving special names to energy that actually still consists of the kinetic and potential energies of individual atoms or molecules.

67. An Important Fact About Potential Energy

The forces responsible for the potential energy of a system, if due to gravitation, are always attractive forces; but, if due to magnetic or electric phenomena, they may be either attractive or repulsive. If the bodies move toward or away from one another, because of these forces, work is done, and potential energy correspondingly decreases. In brief, *when bodies are free to move under mutual attractive or repulsive forces, the potential energy of the system always decreases.*

Illustrations of this principle are observed on every hand:

1. Have a look at a swinging pendulum. At the top of each swing its kinetic energy, for a moment, is zero. But potential energy is then at a maximum. It must thereafter *decrease*, as the pendulum swings downward, under the action of gravitational force. Potential energy is meanwhile being converted into kinetic energy. At the bottom of the pendulum's descent (the mid-point of its swing), potential energy is at a minimum and kinetic energy at a maximum.

2. Where the surface of a liquid touches the walls of a vessel, the surface is curved either upward or downward, into the form that makes potential energy a minimum.

3. The geometric form of a crystal depends on the particular arrangement of its atoms or molecules that makes potential energy a minimum.

4. Why do atoms sometimes combine to form molecules and sometimes fail to combine? Because they may or may not, on close approach, find a position in which the potential energy, due to attractive and repulsive forces between them, is at a minimum.

68. Energy and Work

As a moving body is gradually slowed down, under the influence of any force that opposes its motion, it steadily loses its store of energy. The energy lost is said to have been expended in doing *work* against the opposing force. Energy thus expended is not energy destroyed. If the force overcome is a frictional force the energy expended is merely converted into *heat*. But work done in compressing a spring is stored in the spring as *potential energy;* and work done in setting a body in motion or in making it "gain speed" is converted into *kinetic energy*.

The work done, in any instance, *is measured by the force overcome, multiplied by the distance the body moves through, in the direction in which the force opposes or assists motion*. For example, if the brakes of an automobile resist rotation of the brake-drums with a force of 500 pounds, while the drum surfaces revolve through a distance of 10 feet, the work done by the brakes is 5000 foot-pounds.

In the metric system the force is usually expressed in *dynes* and the distance in centimeters. The energy or work then comes out in *ergs:*

$$\underset{\text{(ergs)}}{Work} = \underset{\text{(dynes)}}{Force\ acting} \times \underset{\text{(centimeters)}}{Distance\ moved\ through}$$

The dyne and erg are extraordinarily small units. The force of gravity, acting on a postage stamp of the most common size, amounts to about 60 dynes. To do an erg of work we would therefore need to lift a stamp through a distance of 1/60 cm, namely, a distance about equal to its own thickness. One may estimate that a fly crawling up a wall must expend many ergs of energy just visibly to move. (Ex. 2–7.)

69. Conservation of Energy

A German physician, Robert Mayer, a little over a century ago (1842) was the first to recognize that *processes and events never create nor destroy energy, but merely change one form of energy into another.* Otherwise expressed, the *total energy of a system of bodies remains unchanged, in spite of all events within the system.* Either of these two statements may be taken as an expression of the *Law of Conservation of Energy*.

Nevertheless, Einstein's discovery (*Principle of Relativity*, 1905) that energy has mass indicates that *matter and energy, under certain circumstances, are interconvertible.* If this is true, then matter and energy are really *conserved jointly*, rather than either of them separately. For example, the energy of the sun must really come from the conver-

sion of matter into energy![1] Calculations show that the energy radiated by the sun corresponds to a loss of mass of about four million tons a second! Fortunately the sun is large enough to endure this prodigal dissipation of its substance for about 1500 million years, before being diminished by as much as 0.01 per cent!

70. Energy Is Conserved When Molecules Collide

We must now pause for just a glimpse of the explanation that science gives for the three *states of matter* (the gaseous, liquid, and solid states). The molecules of a *gas* are relatively far apart, and move unceasingly in all directions, like a swarm of gnats. The fact that a gas may be compressed into a much smaller volume is accounted for by the considerable *free space* between its molecules. The fact that a gas sets up a pressure against the walls of any vessel in which it is contained is explained by unceasing collisions of the swift-moving molecules against the walls of the vessel.

A *liquid*, by contrast, is but slightly compressible, hence we conclude that its molecules are very close together, indeed are almost in contact. But even in a liquid the molecules are in unceasing motion, constantly colliding with one another, and raining down an endless torrent of blows against the walls of the vessel in which the liquid is contained.

The molecules that compose a *solid* are packed still more closely together and are arranged in an orderly manner in space, like bricks in a wall. But they, too, sway back and forth in unceasing motion.

If we ask what keeps the molecules in motion, the answer is that nothing is needed to keep them in motion. They move through empty space. Any influence that they exert upon one another (through electrical or gravitational attraction, or by collision) merely results in one molecule's losing energy that another one gains, hence the total energy of the system of molecules remains unchanged, in agreement with the Law of Conservation of Energy.

71. Heat Energy

The unceasing motion of molecules is in vivid contrast with the motion of bodies that are large enough to be seen or handled. When these are set in motion, experience shows that the motion soon dies

[1] To find the mass in grams corresponding to any given quantity of energy we need only divide the energy, expressed in ergs, by the square of the velocity of light, expressed in centimeters per second, *i.e.*, by $c^2 = 9 \times 10^{20}$.

away. We say that it has been *dissipated by friction* or that it has *disappeared as heat.* But we cannot think of the original kinetic energy as having been destroyed. It must obviously have been transferred to the individual molecules of the moving body, or to those of other bodies over which the moving body slides or with which it collides. The energy having thus been transferred to the molecules (and perhaps in part to the atoms within them), the motion there remains, indefinitely!

To say that the motion of visible and weighable quantities of matter is ultimately dissipated as heat is to say that *heat is the energy of motion of the individual molecules and their component atoms.* Otherwise expressed, *heat is any sort of energy that can be transferred from one molecule to another, in collisions between molecules.* Do not say that the motion of molecules or collisions between them *produces heat.* The motion of molecules *is heat.*

Heat includes (1) the energy of straight-line motion of moving molecules; (2) the energy that the molecules possess in spinning on an axis or tumbling end-over-end; sometimes (3) the energy of atoms, vibrating to and fro within the molecule; (4) potential energy due to attraction of molecules for one another, when they are closely packed together. Since energy of all these sorts may be transferred from one molecule to another, when molecules collide, all of them are included in the heat that a body possesses.

Let us emphasize that heat includes only the *exchangeable* energy of atoms and molecules. If not freely exchanged, in collisions between one molecule and another, it cannot be passed on from a hot body to a cold one, in brief, cannot behave as heat is observed to do. Any motion within an atom or molecule that continues indefinitely, and is not passed on by collision with neighboring molecules or by close approach to them is not included in the heat energy of the body.

72. Heat as Disordered Motion

Heat differs from the motion of large bodies, such as a projectile or flywheel, in that the motion of the molecules is jumbled and confused, whereas the flight of the projectile or the rotation of the flywheel is an ordered motion, all the particles moving together with identical or proportionate velocities, in parallel paths. Thus the common observation that ordinary visible motion tends to take the form of heat simply means that *ordered and regular motion tends to give way to disordered motion,* as if an army, in default of discipline, should disintegrate into a mob.

The difficulty that one finds in getting ordered motion and useful work from heat is simply the difficulty that is always encountered in reducing disorder to order. Experience with molecules as with mobs demonstrates that complete disorder, once attained, never of itself is restored to order. A hot bearing is never observed to cool itself by restoring motion to the wheel. (Ex. 8.)

73. Temperature

When we say that a body is *hot* or has a *high temperature* we do not necessarily imply that it contains a large quantity of heat. We only mean that it has a strong tendency to transfer some of its heat to surrounding *cooler* bodies (those of *lower temperature* than itself). In brief, *temperature is that which determines the direction of transfer of heat between a body and its surroundings.*

But we have said that *heat is any sort of energy that can be transferred from one molecule to another, in collision between molecules.* We can see that it will always be transferred from molecules of high energy to those of lower energy. In other words, *the temperature of a body is a measure of the energy possessed by an average molecule of the body.* Some of its molecules will of course possess more than this average quantity of energy and others less. We can only be sure that the per-molecule average energy of straight-line motion (or any other type of collision-transferable energy) is the same as for any other body of that temperature.

Since temperature measures the per-molecule average transferable energy for a *group* of molecules, there is no such thing as a "hot molecule," though this expression is sometimes loosely used to mean a swiftly moving molecule.

74. Thermometers

A temperature indicator or *thermometer* is anything that indicates changes in temperature by changes in some easily observable property or characteristic, such as color, length, or volume. The color of a piece of hot iron or even that of an incandescent filament or star roughly indicates its temperature.

The length of a column of mercury in a mercury-in-glass thermometer is a convenient indicator of temperature, within the range in which mercury is a liquid. For use at temperatures at which mercury is frozen solid (below −39°C), thermometers are often filled with alcohol or pentane. At still lower temperatures, and even at ordinary tem-

peratures, the electrical resistance (easily measured) of a coil of platinum wire is often used as an accurate measure of temperature. An instrument of this type is often called a *platinum-resistance thermometer*.

75. High-Temperature Measurements

To measure flame or furnace temperatures, special instruments have to be used. Attendants sometimes judge the temperature of a furnace by the color of a piece of steel within it:

Below red heat..........	Below 600°C	Lead melts, 327°C. Zinc melts, 419°C.
Very dull red............	600–700°C	Aluminum melts, 658°C.
Dull red................	700–900°C	Common salt melts, 800°C.
Cherry red..............	900–1000°C	Silver melts, 961°C. Bricks, tile, flower pots, etc., fired.
Orange.................	1000–1100°C	Gold melts, 1063°C. Copper melts, 1085°C.
Yellow.................	1100–1170°C	Roofing tile, stoneware, and porcelain fired.
White..................	Over 1170°C	Steel melts about 1375°C.

Somewhat more precise temperature indications are given by *Seger cones* (sharp-pointed cones made of clay, mixed with varying proportions of other, more or less refractory, materials. Each cone in a numbered series softens and slumps over at a fairly accurately predetermined temperature, provided that it is heated at a predetermined rate. These cones have been used for almost a century for roughly determining conditions (temperature, jointly with rate of heating) in furnaces in which ceramic products are fired.

Still more precise are *thermels* (often called *thermocouples*). Two stout wires of different materials are twisted together to form a "hot junction," which is thrust into the furnace. A feeble electric current is set up in these wires at the expense of heat energy from the furnace. This current swings the needle of a millivoltmeter over a scale that is graduated in degrees.

The temperature of the incandescent interior of a furnace, and even that of the sun or a star, is easily read with an *optical pyrometer*. A telescope is pointed at the incandescent surface, and the brightness of the latter is compared with that of an incandescent lamp filament, whose temperature can be varied by varying an electric current passed through it from a small battery. At sufficiently high temperatures the brightness of a surface depends only on its temperature and not appreciably on the nature of the incandescent material.

76. The Fahrenheit and Centigrade Scales

Thermometers are a modern invention. When they first came into use, in the seventeenth century, a number of different arbitrary temperature scales competed for recognition. Fahrenheit (1686–1736), the inventor of the mercury-filled thermometer, naively assumed that the temperature of a mixture of salt and ice might be the lowest temperature that would commonly or perhaps ever be obtained. So that rather indefinite temperature was made the zero of his scale of temperatures. Then with degrees of a convenient length, measured along the stem of his thermometer, the freezing point of water turned out to be 32°F (degrees *Fahrenheit*) and its boiling point to be 212°F.

The *centigrade* scale has now replaced the Fahrenheit scale in all but English-speaking countries (and even in these, for most scientific work). The freezing point of water in this scale is 0°C, and its boiling point 100°C.

To convert temperatures on one of these scales into those on the other, observe that there are 180 Fahrenheit degrees, but only 100 centigrade degrees in the interval between the freezing point and the boiling point of water. So each degree on the Fahrenheit scale is only $\frac{100}{180} = \frac{5}{9}$ of a degree on the centigrade scale. So we have the rules:

$$°C = (°F - 32) \times \tfrac{5}{9} \qquad\qquad °F = (°C \times \tfrac{9}{5}) + 32$$

77. The Absolute Scale

As a body is cooled to lower and lower temperatures the motion of its molecules is continuously slowed down. Finally, we approach the lowest possible temperature, called *absolute zero*. At absolute zero a body would be completely devoid of heat and its molecules would possess no motion that they could pass on to other molecules, in colliding with them. (The molecules of solid hydrogen have been proved still to *rotate* at absolute zero.)

Now a *completely logical temperature scale* ought to have its zero at absolute zero. Above that temperature its readings ought to be proportional to the thing that temperature is supposed to measure, in other words to the *transferable energy of any particular kind, for an average molecule.* Doubled temperature, for example, would mean that an average molecule possessed twice the energy of straight-line motion that it did before.

Such a completely logical temperature scale would not be defined in terms of any particular substance, hence might be called *an absolute*

scale. But when we attempt to measure temperatures on such a scale we must choose an appropriate "thermometric substance." Neither

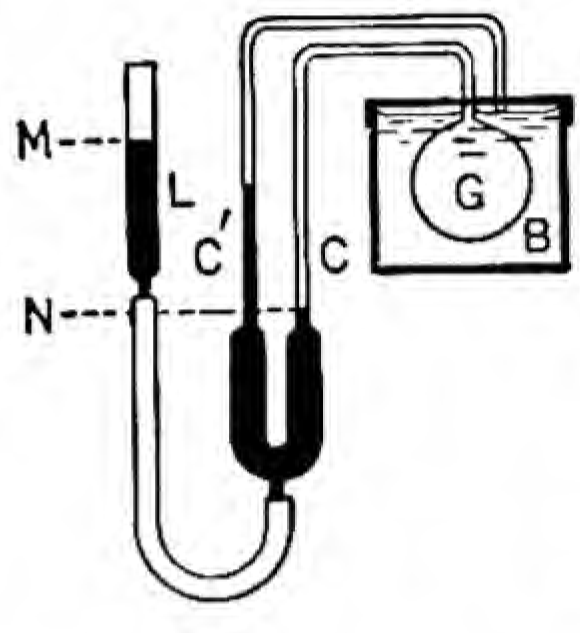


FIG. 16 Gas thermometer. Hydrogen or nitrogen is confined within a constant volume in a container, *G*, heated to a uniform temperature in a bath, *B*. To correct for expansion or contraction of gas within the connecting capillary, *C*, an exactly similar capillary, *C'*, is placed beside *C*. Then by bringing the mercury in both capillaries to the same level, *N*, we can make sure that the volume of gas within the container has remained constant (except for a slight change in volume, easily corrected for, of *G* itself). The difference between the two mercury levels, *M* and *N*, when added to the barometer, gives the total pressure under which the gas is confined. This pressure is proportional to the absolute temperature, for an ideal gas, whenever the volume of the gas is kept constant.

mercury nor any other liquid would serve very well, since the expansion of a liquid, from one degree to the next, is not quite the same for all points of the logical temperature scale. Gases that are difficult to condense expand more uniformly than any liquid. If they are greatly *rarefied* (greatly expanded in volume because confined under very low pressures) they are better yet.

So we conceive of a thermometer filled with an imaginary *ideal gas*, which would expand uniformly at all points of the logical temperature scale. *Real gases, when confined under low pressures, are very nearly ideal.* In practice, such difficultly condensible gases as hydrogen and nitrogen are sufficiently nearly ideal, even under ordinary pressures, to permit them to be used in *gas thermometers* (Fig. 16).

Actually, gas thermometers are too cumbersome to be used in everyday affairs. Probably hardly a dozen of them exist in all the world. They have been used by the National

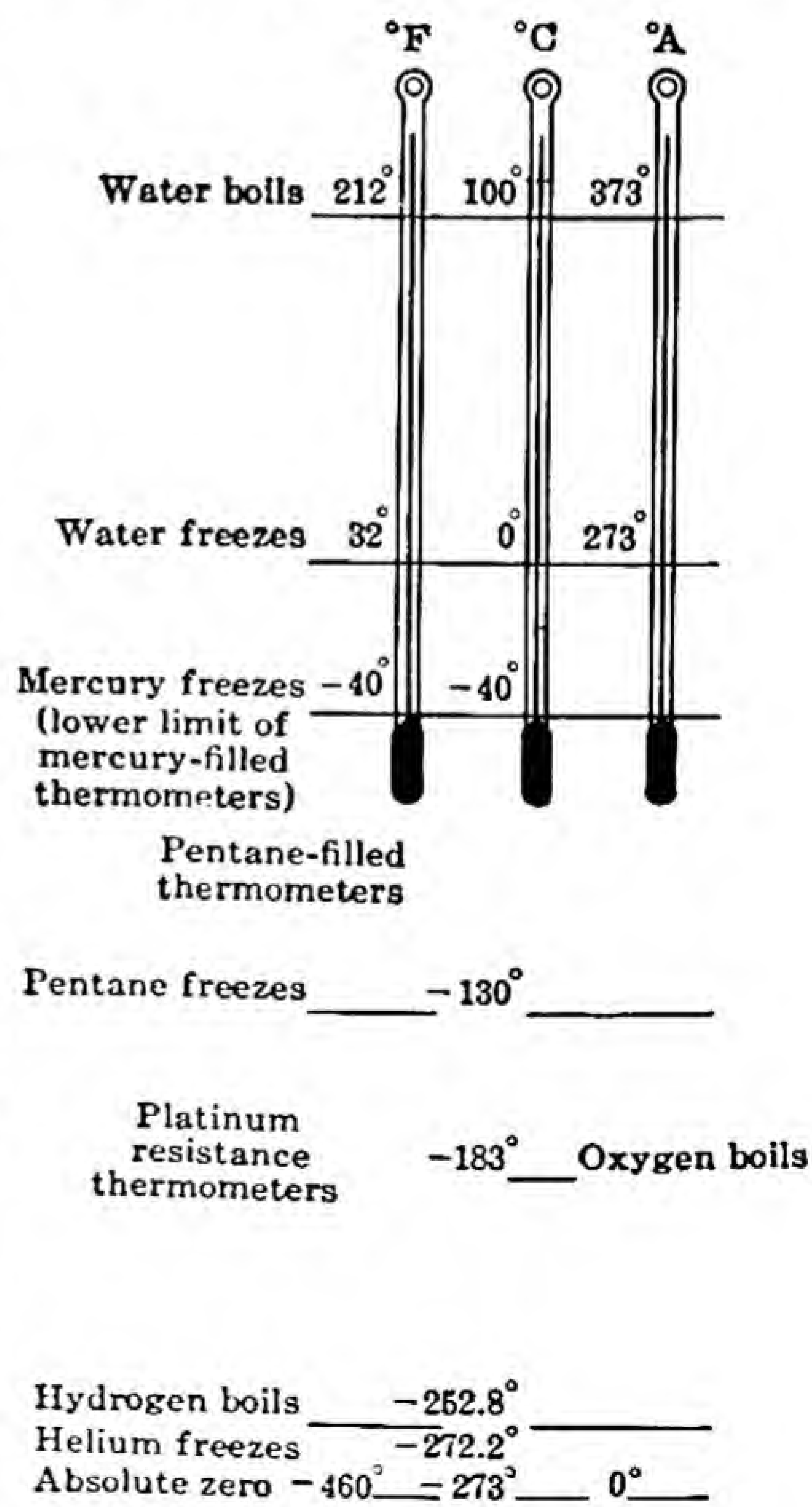


FIG. 17.

Bureau of Standards, in Washington, and by similar institutions in other countries, to establish *primary fixed points*, such as the temperatures at which water freezes, water boils, tin melts, and sulfur boils.

Intermediate temperatures may then be established with the aid of *platinum-resistance thermometers*, based on variation of the resistance of a coil of fine platinum wire with varying temperature. Finally, ordinary mercury-in-glass thermometers may be checked at various points against true temperatures on the absolute scale, as read from the platinum-resistance thermometers. They may then serve as *standard thermometers*, for *calibrating* others.

On the *ideal gas temperature scale*, usually called *the absolute* or *Kelvin* scale (from its inventor, Lord Kelvin, 1848), the interval between the freezing and boiling points of water is arbitrarily taken as 100 degrees, just as on the centigrade scale. Then water is found to freeze at 273.16°A (or °K) and to boil at 373.16°A (or °K). So

$$°\mathrm{A} = °\mathrm{C} + 273 \qquad\qquad °\mathrm{C} = °\mathrm{A} - 273$$

nearly enough for most purposes. The three temperature scales are compared in Fig. 17.

78. Heat Is Measured in Calories or Btu

Two quantities of heat are said to be equal when they produce identical results—for example, when they will melt equal quantities of ice, or will heat a definite mass of water from some chosen lower temperature to the same upper temperature.

The practical unit of heat is the *calorie* or gram calorie (more precisely called the 15° calorie). This is the quantity of heat needed to raise the temperature of *1 gram of water from 14.5° to 15.5°C.*, or, in ordinary practice, with sufficient accuracy, from any temperature to another that is 1 degree higher, on the centigrade scale. (To raise the temperature of a gram of water from 14.5° to 15.5° on the centigrade scale does not require exactly the same amount of heat as is needed from 19.5° to 20.5°, though the difference is small, and commonly neglected.)

A *kilogram calorie* or *kilocalorie* is 1000 calories. It is more convenient than the calorie for dealing with large amounts of heat.

In engineering practice the unit of heat is the *British thermal unit* (Btu). This is the quantity of heat needed to heat a pound of water from 39° to 40°F. 1 Btu = 252 calories. (Ex. 9.)

79. Heat Capacity and Specific Heat

Whenever heat is added to any body a part of it is used to rouse the atoms and molecules of the body into more violent motion. This part is really still present, within the body, as *heat*. If the body is permitted to *expand* on being heated, some additional heat energy must be put into the body to perform work (*external work*, in pushing back the atmosphere, as the body expands; and *internal work*, in overcoming the attraction of the molecules for one another). This work is really stored as potential energy of the system (body + surroundings).

Different substances differ greatly in the amount of heat absorbed by samples of equal weight, in being heated through any specified range of temperature. This obviously means that the heat motion of certain substances is more complicated than that of others, because it includes not only straight-line motions of molecules but also spinning or tumbling motions, and often potential energy, due to attractive forces between neighboring atoms and molecules. When we add heat to a body we rouse into activity all the different sorts of motion of which its molecules are capable at that temperature; *the more types of motion are possible the more heat will be needed to increase the temperature of the body any specified amount.*

By the *heat capacity* of a material we mean the number of calories absorbed by *any specified weight* of it, in having its temperature increased 1 degree centigrade. *Specific heat* refers to the heat capacity of 1 *gram* of material. The heat capacity and specific heat of nearly all substances increase with increasing temperature. (Ex. 10, 11.)

80. How to Determine the Quantity of Heat Liberated in the Combustion of a Fuel

To find out how much heat is liberated in combustion of coal or some other solid or liquid fuel, a weighed sample is burned in a thick-walled "calorimeter bomb" (Fig. 18), constructed of an oxygen-resistant and acid-resistant alloy (*illium*, § 499), and closed with a heavy screw cap. A carefully weighed sample of the fuel is placed in a small platinum cup at *A*, in contact with a fine iron wire, which is connected through two heavy conductors and the terminals at *B* with a pair of storage cells. Pure oxygen under pressure of about 20 atmospheres is introduced through the valve *V*, at the top. The bomb is then immersed in a known quantity of water in a covered, insulated vessel, supplied with a delicate thermometer, as shown in Fig. 19.

When all is ready, the combustible substance in the bomb is ignited by closing the electric circuit for a moment. In the atmosphere of compressed oxygen the fine iron wire and the fuel sample itself are instantly burned, liberating a definite quantity of heat, which goes to raise the temperature of the water and bomb. After the water has been stirred for several minutes the total rise in temperature may be noted.

The bomb itself, from its known specific heat (§ 79), is rated as the equivalent of some definite weight of water. Adding this "water

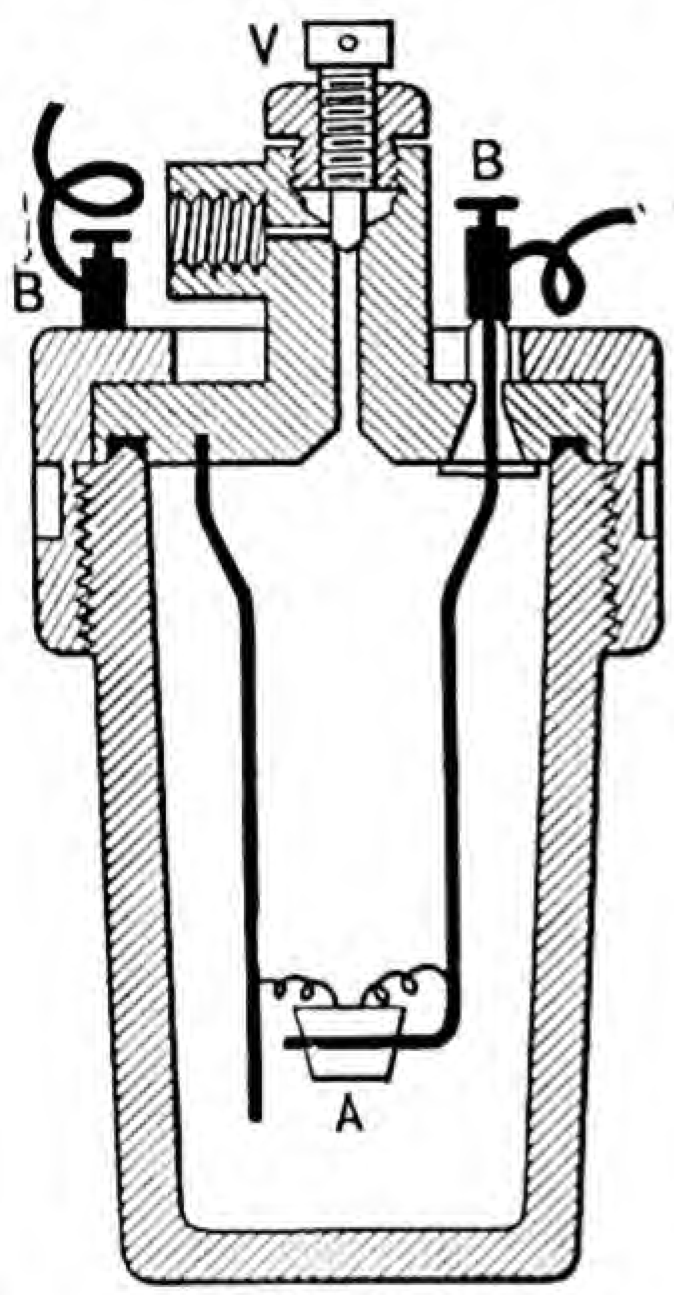


FIG. 18. Calorimeter bomb.

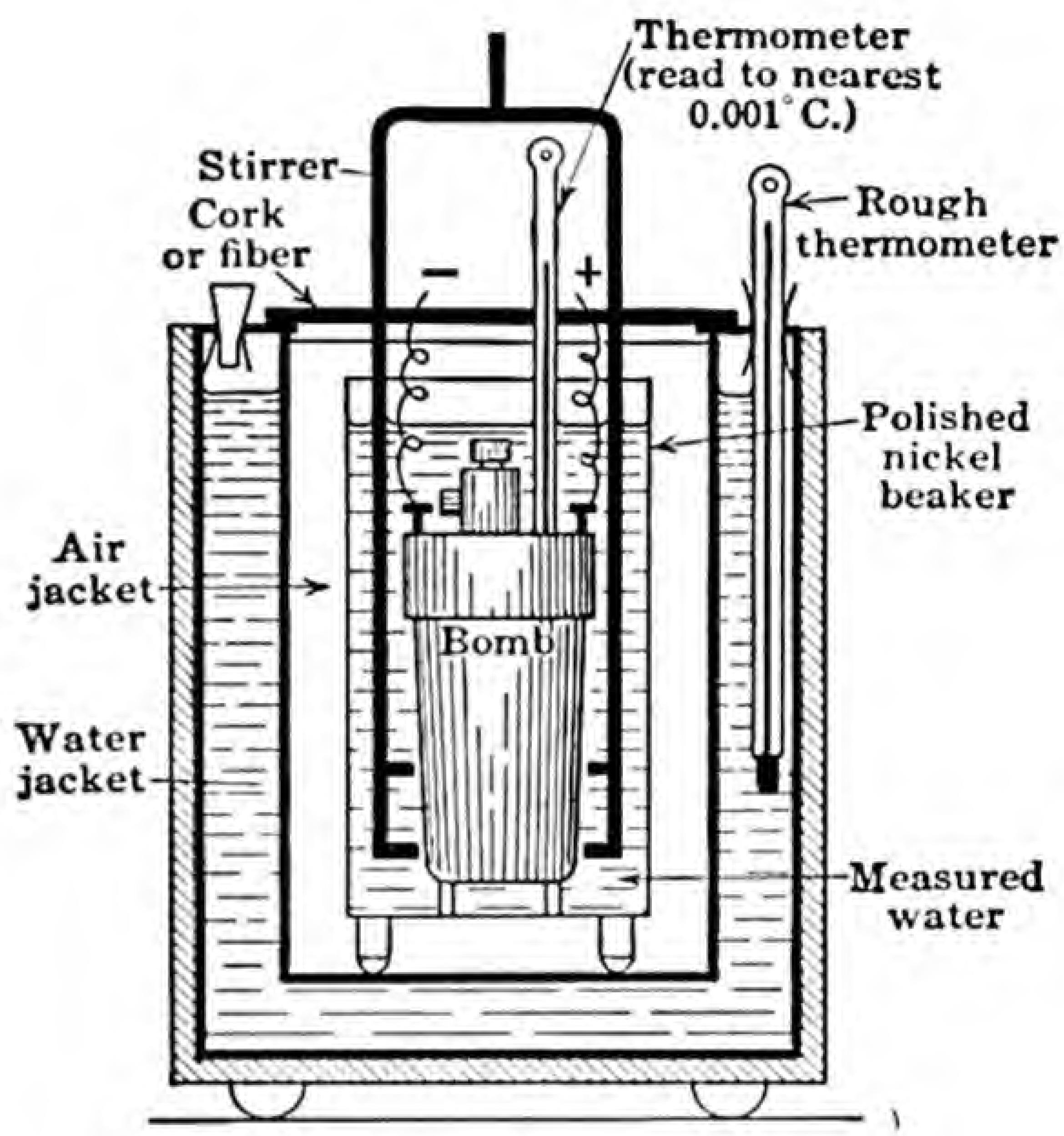


FIG. 19. Calorimeter.

equivalent of the bomb" to the weight of water surrounding the bomb, we get a total weight, which needs only be multiplied by the observed rise in temperature to give the total number of calories liberated by the burning. In practice, of course, a correction must be made, not only by deducting the heat liberated by the combustion of the fine iron wire, but also by adding heat estimated to have been lost by being carried away by conduction through the thermometer and stirrer and the outer walls of the apparatus.

To make sure that the principle is understood the student should pause, now, to carry through a typical calculation. (Ex. 12.)

81. Fuel Values

The heat liberated by the combustion of 1 *gram* or 1 *pound* of a fuel in a calorimeter is often referred to as the *fuel value* of that material.

We should remember, however, that the quantity of heat obtained when a fuel is burned under a boiler is definitely less than that obtained in a calorimeter. Combustion under a boiler may be *incomplete*, owing to insufficient oxygen being present; and considerable heat is carried up the chimney by the hot gaseous products of combustion. Moreover, a little extra heat is liberated in a calorimeter, for the bomb is surrounded with cold water, which causes most of the water vapor produced in combustion to be condensed to liquid, with consequent liberation of heat.

Other types of calorimeters have been devised for determining the heat liberated in burning a gaseous fuel or in a chemical reaction between dissolved substances.

82. Exothermic and Endothermic Reactions

Reactions that liberate heat are often said to be *exothermic*. The amount of heat liberated cannot be calculated in any way, but needs to be determined by actual trial with a calorimeter, as just described.

A few reactions fail to liberate heat, but on the contrary cause heat to disappear. Reactions of this sort are said to be *endothermic*. A constant supply of heat from some outside source is necessary to keep them going. You may, if you wish, view the heat that disappears as being stored up in the products of the reaction as chemical energy, which in some subsequent chemical reaction is perhaps again converted into heat.

When heat disappears in an endothermic reaction it is withdrawn from the immediate surroundings of the reacting materials, hence the surroundings tend to be cooled. Endothermic reactions, because they remove heat from the surroundings, are sometimes said to *absorb heat;* but do not get the notion that the heat absorbed is in some way made to raise the temperature of the reactants or reaction products. The exact reverse is true: Since heat *disappears* in such reactions, being converted into chemical energy, the material and surroundings remain at a lower temperature than would otherwise be attained.

The student may wonder why most reactions liberate heat, whereas a few cause heat to disappear. The answer is not hard to find:

1. Reactions of *direct union* decrease the number of molecules present. All the energy that the system formerly contained must now be distributed among a smaller number of molecules. In other words, the *per-molecule average energy* must be higher, that is to say, the *temperature* must be higher. Reactions of direct union are thus nearly always *exothermic*.

2. When molecules draw close to one another and the atoms within them are regrouped into new types of molecules, there is always *a decrease in potential energy* (§ 67). The energy thus released is handed on from molecule to molecule, in collisions between them, and is thus converted into the confused molecular motion that we call heat. So most reactions liberate heat, whether they are reactions of direct union or not.

3. In some instances, however, the newly created molecules are so *numerous*, in comparison with the original molecules, or are capable of such *complicated motions* that there is a considerable demand for energy, just to give them all the per-molecule average energy that corresponds to the temperature. If this demand for energy is more than is supplied by the decrease in potential energy the temperature must fall. This is an *endothermic* reaction.

Technical Words

Force—an interaction between two or more bodies which tends to accelerate them toward or away from one another.

Work—the product *force* × *distance*, when a body moves through a definite distance, impelled to move by a force, or in spite of the opposition of a force. (Work is said to be done "on the body" when the force acts to impel motion, and to be done "by the body" when the force acts to oppose its motion.)

Dyne—the metric unit of force; it is the force which, acting on a body of 1-gram mass, free to move, will increase or decrease the velocity of the body by *1 centimeter per second, for each second that the force acts.*

Erg—the work done by a force of 1 dyne, acting upon a body while this moves 1 centimeter, in the direction in which the force is applied.

Matter, p. 69. **Energy,** p. 69. **Radiant energy,** p. 69.

Kinetic energy, p. 70. **Potential energy,** p. 70.

Heat, p. 74. **Temperature,** p. 75. **Thermometer,** p. 75.

Thermel or **thermocouple,** p. 76. **Calorie,** p. 79. **Kilocalorie,** p. 79.

Heat capacity, p. 80. **Specific heat,** p. 80. **Fuel value,** p. 81.

Exothermic, p. 82. **Endothermic,** p. 83. **Absolute zero,** p. 77.

Calibrate—to determine the corrections to be applied to the readings of any instrument, such as a thermometer, to make them conform to some accepted standard.

Calorimeter—any instrument for measuring the quantity of heat set free or disappearing in a physical or chemical process.

Pyrometer—any instrument for measuring high temperatures.

Primary fixed points (of a thermometric scale)—a set of widely spaced temperatures, representing easily determined melting points and boiling points, which are used in the calibration of thermometers.

Ideal gas scale—a temperature scale in which temperatures are made proportional to the *volume* (constant pressure) or the *pressure* (constant volume) of an ideal gas.

Absolute scale—any temperature scale that is independent of the properties of individual substances, but is defined, instead, in terms of theoretical views of temperature or heat. In practice, it is so defined as to be identical with the ideal gas scale.

Summary

§ 65. What we mean by energy and by work.

§ 66. What we mean by kinetic energy. A formula for calculating kinetic energy. Units employed in applying this formula.

What we mean by potential energy. What radiant energy is.

§ 67. What happens to the potential energy of a system if the bodies composing the system are free to move.

§ 68. How work done may be calculated. Units used in the calculation.

§ 69. A statement of the Law of Conservation of Energy. The source of the sun's energy; why this is not considered a violation of the Law of Conservation of Energy.

§ 70. What keeps molecules in motion.

§ 71. A statement of what we mean by heat, emphasizing energy transfer. Four types of energy included in heat.

§ 72. Why ordinary, visible motion tends to take the form of heat.

§ 73. Temperature, defined in terms of direction of heat transfer. Temperature, defined in terms of molecules.

§ 74. Several different qualities of bodies, sometimes used to indicate temperature. How very low temperatures are measured.

§ 75. Four different methods for measuring high temperatures.

§ 76. The freezing and boiling point of water on the Fahrenheit and centigrade scales. Rules for converting temperatures on either of these scales into temperatures on the other.

§ 77. What we mean by absolute zero. Motion of molecules at absolute zero.

Two requirements for a completely logical temperature scale. What real substances most nearly expand at uniform rate, over all parts of the logical temperature scale. What imaginary substance would do so exactly.

Conditions under which real gases are most nearly ideal. Definition of the absolute or Kelvin scale.

What gas thermometers are used for. What easily reproducible temperatures are used to establish primary fixed points in calibrating thermometers. What we mean by calibrate (p. 83).

§ 78. How we may determine that two quantities of heat are equal.

Definitions of the metric and engineering units of heat.

§ 79. Ways in which the heat put into a body may be used.

Why different substances differ in the amount of heat required to heat equal weights of material through any specified range of temperature.

Name given to the quantity of heat, in calories, required to increase the temperature of any specified weight of material 1 degree centigrade; and to increase the temperature of 1 gram of material 1 degree centigrade.

§ 80. A description of a bomb calorimeter. An explanation of how it is used, and how the heat liberated may be calculated from the observed rise in temperature.

§ 81. What is meant by fuel value. Why the heat liberated in burning a fuel under a boiler may be much less than that indicated by its fuel value.

§ 82. Name given to reactions that liberate heat. Name given to reactions in which heat disappears.

A brief explanation of why heat is set free in exothermic reactions. Why heat disappears in endothermic reactions.

Exercises

Before beginning these exercises, the student should familiarize himself with the most important metric units, Appendix A.

1. A body with a mass of 100 grams moves with a velocity of 10 cm per sec. What is its kinetic energy, in ergs? 500

2. Two joules (20,000,000 ergs) of energy will impart what velocity to a kilogram mass, originally at rest? 200

3. A force of 100 dynes is applied to *assist* the motion of a body while the body moves 1 meter (= 100 cm) in the direction in which the force impels motion. Does the body gain or lose energy? How many ergs of energy? Is work done *on* the body or *by* the body (p. 83)? 100

4. A joule is 10,000,000 ergs. If a body moves in the direction in which a force impels motion, while 1 joule of work is done on it, does it gain or lose energy, and how much? If it moves 10 meters (convert into centimeters) while the joule of work is done on it, what is the acting force, in dynes? 100

5. The force of gravity, acting on a 1-gram mass, amounts to 981 dynes. What will it be for a kilogram mass?

How much work, in ergs, must be done in lifting a kilogram mass vertically, against the force of gravity, through a height of 1 meter (convert to centimeters)? Does this body gain or lose energy in being lifted? How many ergs and how many joules? 981

6. A body having a kinetic energy of 10,000 ergs moves 10 meters (convert into centimeters) while being brought to a stop by a force. What is the force, in dynes?

7. A compressed, coiled spring contains 981,000 ergs of potential energy. Through what height will it lift a gram, assuming that the force of gravity on a gram-mass is 981 dynes? 100

8. The "surface energy" of a soap bubble is obviously due to attractive forces between its particles. Is it potential or kinetic? What becomes of this energy when the bubble bursts?

9. A gram of steam, condensing to water at 100°C, liberates 540 calories of heat. Figured roughly, how many Btu is this for each pound of steam condensed? (1 lb = 454 grams.) 970

10. The specific heat of lead is roughly 0.03. What weight of lead must cool from 220° to 20°C in order to raise the temperature of a liter of water 1 degree centigrade? 167

11. What is the specific heat of a substance, if a 100-gram sample has its temperature raised 30 degrees by the condensation of 1 gram of steam? (See Exercise 9.)

12. In an experiment with a bomb calorimeter, the bomb was known to have the same heat capacity as 60 grams of water. It was submerged in 500 cc of water (nearly enough, 500 grams). If the rise in temperature was 3.4°C, how many calories were liberated (neglecting losses)? 190

Chapter 7

HYDROGEN

The atom and molecule of hydrogen are the lightest of any known. For this reason hydrogen may be regarded as the simplest form of matter. Its presence (combined with other elements) in *water*, in *acids*, and in the multitude of compounds contained in *living plants and animals* gives it special importance. After oxygen, hydrogen is the most abundant element in the earth's crust, if we rate abundance by numbers of atoms, rather than by actual weights.

► 83. Occurrence of Hydrogen

Hydrogen in an *elementary condition* (*i.e.*, free or uncombined) occurs in the earth's atmosphere only in traces. Nevertheless, enormous quantities of elementary hydrogen are found in the atmosphere of the sun; and during solar eclipses red flames or eruptions of incandescent hydrogen (the "solar prominences") may be observed, darting out from the solar rim for several hundred thousand miles (Fig. 20).

Hydrogen, in combination with other elements, is found in thousands of compounds:

Elements	*Important Compounds or Mixtures Containing These Elements*
H, O	Water (one-ninth hydrogen by weight)
H, N	Ammonia (NH_3)
H, C	*Hydrocarbons.* Examples: Petroleum, gasoline, lubricating oil; turpentine, rubber; methane (CH_4) and other hydrocarbon gases
H, C, O	Wood, paper; starches, sugars, fats; alcohols, ethers, aldehydes, organic acids; thousands of other organic compounds
H, C, O, N (often other elements)	The protein part of our foods; alkaloids (such as quinine, nicotine, and strychnine); many dyes and medicinal substances
H, non-metals	Acids
H, metals	Sodium hydride, NaH; calcium hydride, CaH_2; and others

Courtesy of Yerkes Observatory

FIG. 20. A part of the sun's rim, showing solar prominences. White dot represents comparative size of the earth.

84. Preparation of Hydrogen by Decomposing Its Compounds

To prepare any element in the free or uncombined condition, certain of its compounds may be decomposed, by being heated or by electrolysis. Thus we may prepare hydrogen:

1. By decomposing *ammonia gas*, by passing it through a hot copper tube:

$$2NH_3 \rightarrow N_2 + 3H_2$$

This is a convenient method for obtaining large quantities of hydrogen gas (mixed with nitrogen) in the laboratory, since the ammonia may be drawn from a cylinder of liquid ammonia. When hydrogen is to be used as a reductant (§ 93) its being mixed with moderate amounts of the relatively *inert* (unreactive) gas, nitrogen, is no disadvantage.

2. By *electrolysis of water:*

$$2H_2O \rightarrow 2H_2 + O_2$$

This method yields very pure hydrogen, for the two products of the electrolysis are liberated at separate electrodes (Fig. 9, p. 48) and are separately collected.

3. By decomposing *petroleum* (a complex mixture of liquid hydrocarbons) at high temperatures, in the presence of catalysts. This is the *cracking process* for the production of motor fuels from petroleum (§ 460). As *by-products* (products obtained in addition to those chiefly desired), this reaction yields combustible hydrocarbon gases and considerable quantities of hydrogen. Since millions of tons of petroleum are cracked every year, petroleum refinery gases are one of the most important sources of hydrogen gas, for its industrial uses. (Ex. 1–3.)

85. Relative Volumes of Gases Concerned in a Chemical Reaction

The equation

$$\begin{array}{lcccccc} & 2NH_3 & \rightarrow & N_2 & + & 3H_2 \\ \text{Molecules:} & 2 & & 1 & & 3 \\ \text{Volumes:} & 2 & & 1 & & 3 \end{array}$$

shows that two molecules of ammonia are decomposed to obtain one molecule of nitrogen and three molecules of hydrogen. By Avogadro's Principle, equal numbers of molecules occupy nearly equal volumes. So, with twice as many *molecules* of ammonia as of nitrogen, it is plain that the *volume* of the ammonia must be twice that of the nitrogen. Similarly, with three molecules of hydrogen for each molecule of nitrogen, the volume of the hydrogen must be 3 times that of the nitrogen. So, in the mixture of gases obtained by decomposing ammonia gas, nitrogen makes up 1 volume in 4, and thus is 25 per cent of the mixture, by volume; whereas hydrogen makes up 3 volumes in 4 and is 75 per cent of the mixture, by volume.

As a second example, consider the electrolysis of water. The equation

$$\begin{array}{lcccccc} & 2H_2O & \rightarrow & 2H_2 & + & O_2 \\ \text{Molecules:} & & & 2 & & 1 \\ \text{Volumes:} & & & 2 & & 1 \end{array}$$

shows that this produces two molecules of hydrogen for each molecule of oxygen. The volumes, by Avogadro's Principle, must be in the same proportion. So, whatever volume of oxygen is obtained, we should obtain twice that volume of hydrogen. This checks an observation we made in an earlier chapter (§ 45, item 5).

Water is a *liquid*, hence Avogadro's Principle does not apply to it. But if it were *water vapor*, the equation just considered shows that the number of molecules of water vapor would be the same as the number of molecules of hydrogen, hence their volumes would be equal.

Finally, consider the complete combustion of methane:

$$\begin{array}{lcccccccc} & CH_4 & + & 2O_2 & \rightarrow & CO_2 & + & 2H_2O & \text{(vapor)} \\ \text{Molecules:} & 1 & & 2 & & 1 & & 2 & \\ \text{Volumes:} & 1 & & 2 & & 1 & & 2 & \end{array}$$

It is evident that the volume of oxygen needed is twice the volume of the methane burned. The volume of the carbon dioxide produced is the same as that of the methane. The volume of the water vapor produced is twice that of the methane. But if the water vapor were condensed to liquid its volume would be negligibly small.

To summarize: *The volumes of gases and vapors concerned in a chemical reaction are in the same ratio as the numbers of molecules in the balanced chemical equation.* This is best kept in mind as a practically useful rule, and not thought of as an independent law. It is only an

obvious consequence of the fact that equal numbers of molecules occupy equal volumes. (Ex. 4–6.)

Does the total volume increase, decrease, or remain constant in each of the following reactions involving gases?

$$H_2 + Cl_2 \rightarrow 2HCl$$

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl$$

$$CO + 2H_2O \text{ (vapor)} \rightarrow CH_3OH \text{ (vapor)}$$

$$2CO + O_2 \rightarrow 2CO_2$$

Since the numbers of molecules appearing in a balanced chemical equation are small whole numbers, the relative volumes of gases are, too. This is the *Law of Gay-Lussac:* The volumes of gases transformed or produced in any chemical reaction are in the ratio of small whole numbers.

86. Preparation of Hydrogen by Displacement from an Acid

An element may not only be secured in the free or uncombined state by *decomposing* certain of its compounds (§ 84) but also, very frequently, *by causing a more active element to displace it from its compounds.* In the preparation of hydrogen by displacement, the displacing element is usually a *metal* (though the non-metals carbon, silicon, boron, and even sulfur will serve); and the compound from which it displaces hydrogen is usually an *acid* or *water.*

Any active or fairly active metal will displace hydrogen from acids. Zinc is more commonly used than any other metal, and the acid used is commonly dilute hydrochloric or sulfuric acid:

$$Zn + 2HCl \rightarrow \underset{\substack{\text{Zinc}\\ \text{chloride}\\ \text{(a salt)}}}{ZnCl_2} + H_2\uparrow$$

$$Zn + H_2SO_4 \rightarrow \underset{\substack{\text{Zinc}\\ \text{sulfate}\\ \text{(a salt)}}}{ZnSO_4} + H_2\uparrow$$

In a previous chapter we recognized as acids *all substances that turn blue litmus red.* Now we have another and more fundamental property by which an acid may be recognized: *Acids, reacting with active metals, usually liberate hydrogen gas.* By this test even water is an acid, though one so feeble or slightly active that it fails to affect litmus. The most familiar acids all contain hydrogen, together with one or more other elements.

When an acid reacts with a metal, liberating hydrogen gas, the other product formed is called a salt. Any salt produced by the action of an

acid on a metal will contain that metal, together with a non-metal or a group of non-metals, derived from the acid.

Let M stand for a metal and X for a non-metal, or a group of non-metallic atoms. The reaction of the metal with an acid, liberating hydrogen, may then be written:

$$\underset{\text{Acid}}{HX} + \underset{\text{Metal}}{M} \rightarrow \underset{\text{Salt}}{MX} + \underset{\text{Hydrogen gas}}{\tfrac{1}{2}H_2}$$

in which $\frac{1}{2}H_2$ expresses the fact that hydrogen gas is always set free as molecules of the formula H_2, half of such a molecule being obtainable from every acid molecule of the formula HX. (If desired, one might double the whole equation, and so get rid of the fraction.) (Ex. 7–9.)

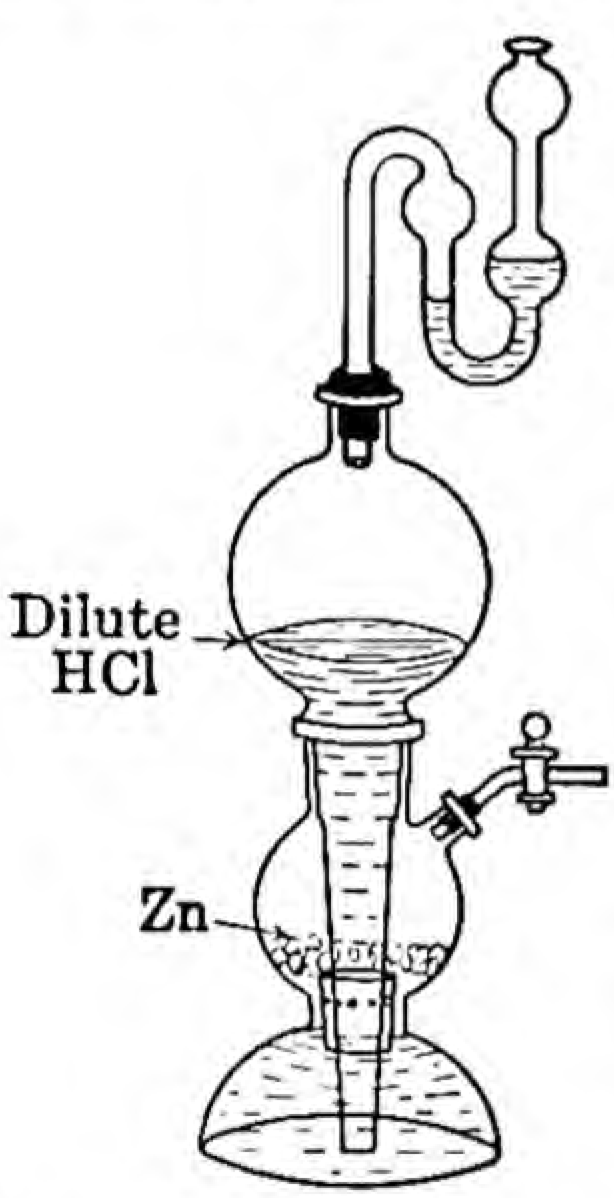


FIG. 21. Kipp generator.

When hydrogen is generated as just described it is usually drawn from a Kipp generator, shown in Fig. 21. The middle compartment contains zinc, which is placed on a perforated shelf or a layer of glass wool. Dilute hydrochloric acid, descending from the upper compartment through its elongated stem, fills the lowest compartment and then, rising a little higher, comes in contact with the zinc.

Hydrogen escapes through the stopcock. But when the stopcock is closed the pressure of the gas, continuing to collect in the middle compartment, forces the acid downward into the lower compartment, whence it rises into the upper reservoir. When acid no longer makes contact with the zinc the reaction stops. Thus hydrogen may be obtained *intermittently*, as desired (instead of being evolved continuously), until either the zinc or the acid is exhausted.

87. Preparation of Hydrogen by Displacement from Water

The most active metals (those nearest the top of the list on p. 92) displace hydrogen even from water. The result is hydrogen and a metallic hydroxide (alkali).

1. Metallic sodium, potassium, calcium, and several other less common *light metals* react rapidly with water, even at room temperature:

$$\underset{\text{Sodium}}{2Na} + \underset{\text{Water}}{2HOH} \rightarrow \underset{\text{Sodium hydroxide}}{2NaOH} + H_2\uparrow$$

$$\underset{\text{Calcium}}{Ca} + 2HOH \rightarrow \underset{\text{Calcium hydroxide}}{Ca(OH)_2} + H_2\uparrow$$

We have represented water, here, by the formula HOH, to indicate that only half of its hydrogen is displaced by sodium or other active metals, the other half remaining in the group of atoms OH (often called the *hydroxyl group*), which is still present in one of the final products.

When the experiment just described is performed on a small scale in the laboratory, step back a few feet, for the reaction sometimes ends in a small explosion. The solution that is produced has an

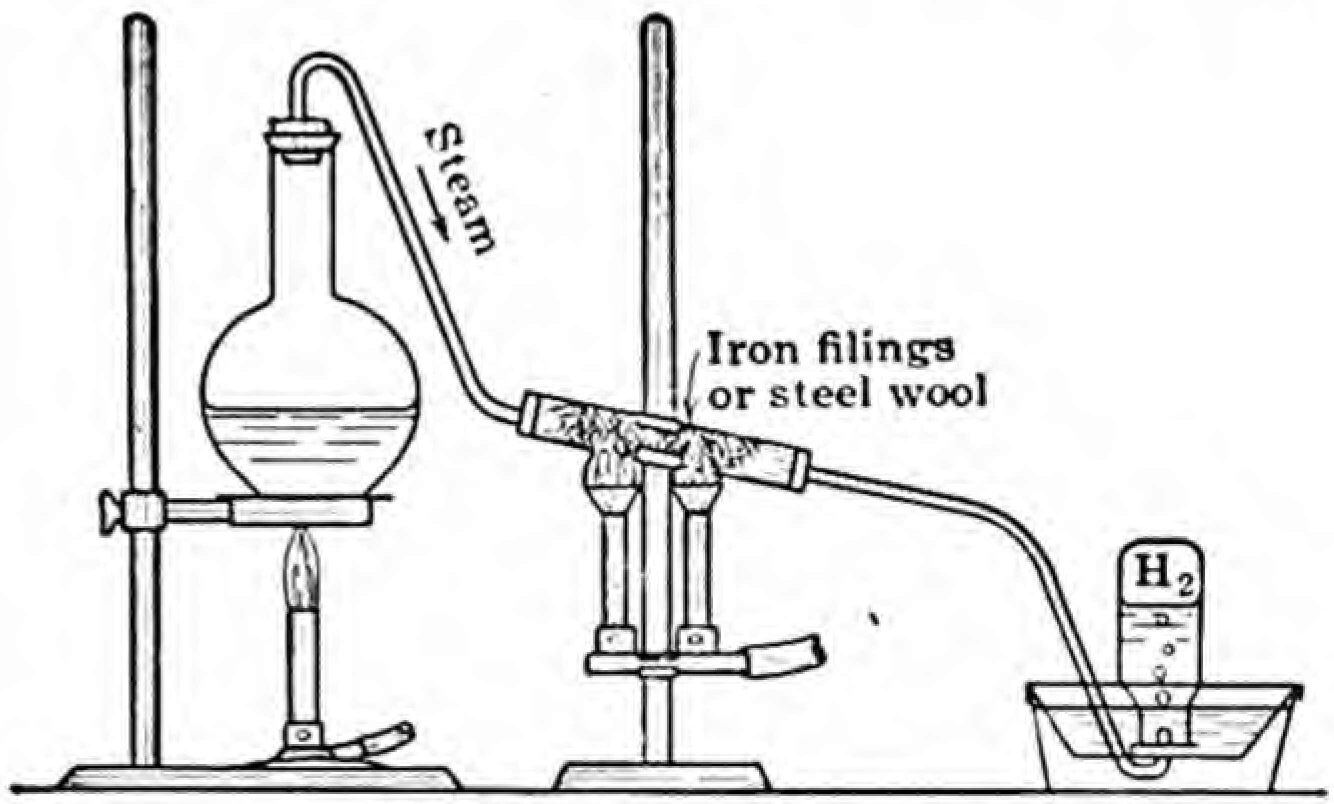


FIG. 22. Reaction of iron with steam.

alkaline reaction (turns red litmus blue), thus showing that a *soluble metallic hydroxide* (often termed an *alkali*) is one of the products. (Ex. 10, 11.)

2. Iron, when strongly heated, displaces hydrogen from steam (Fig. 22), and is converted into *magnetic iron oxide:*

$$\underset{\text{Iron}}{3Fe} + \underset{\text{Steam}}{4H_2O} \rightarrow \underset{\substack{\text{Magnetic} \\ \text{iron oxide}}}{Fe_3O_4} + 4H_2\uparrow$$

Observe that in this reaction all the hydrogen of the water is displaced, so that the solid product is an oxide rather than a hydroxide.

3. White-hot coke or charcoal (impure forms of carbon) will displace hydrogen from steam. The other product is a gas, carbon monoxide:

$$C + H_2O \rightarrow \underbrace{CO\uparrow + H_2\uparrow}_{\text{Water gas}}$$

The mixture of carbon monoxide and hydrogen thus obtained is called *water gas*. The two gases are readily separated by oxidizing the carbon monoxide, in the presence of a catalyst, to carbon dioxide, which is then dissolved in water (under pressure), leaving the hydrogen undissolved. Water gas is one of the most important sources of hydrogen for the industries that use hydrogen as a raw material (§ 94).

► 88. The Activity Series of the Metals

At the bottom of this page is an **activity series,** also often called a **displacement series** or **electrochemical series.** It is a list of substances (here a list of *metals*) arranged in the order of *decreasing chemical activity.*

1. Metals near the top of the series (sodium, potassium, etc.) are so active that they react with active acids, liberating hydrogen, with *dangerous violence;* even with water they react vigorously.

2. Magnesium, aluminum, zinc, etc., farther down the list, react with acids *less vigorously;* with water they react only very slowly, unless the water is boiled (magnesium, aluminum) or passed over the heated metal in the form of steam. (Ex. 12–14.)

3. Cobalt, nickel, tin, and lead, still farther down the list, react with steam only very slowly, if at all; with the most active acids they still react, liberating hydrogen.

1. Very active (react even with cold water; react violently with acids)	Li	1. Oxides not reduced by hydrogen or carbon monoxide but only by electrolysis or by heating with the most active metals
	K	
	Ba	
	Sr	
	Ca	
	Na	
2. Less active (react with steam or acids)	Mg	
	Al	
	Mn	2. Oxides reduced by carbon or aluminum at high temperatures, but not by hydrogen or carbon monoxide
	Zn	
	Cr	
	Cd	
	Fe	3. Oxides reduced by hydrogen or carbon monoxide at high temperatures
3. Moderately active (react with acids, liberating hydrogen)	Co	
	Ni	
	Sn	
	Pb	
	H	
4. Slightly active (react only with oxidizing acids, or with other acids in the presence of plentiful supply of air)	Cu	
	As	
	Bi	
	Sb	
	Hg	4. Oxides decomposed by heat
	Ag	
5. Least active (dissolve only in aqua regia and in a few other very powerful oxidants)	Au	
	Pt	

4. Copper, mercury, silver, etc., *next below hydrogen* in the series, do not react with acids to liberate hydrogen at an appreciable rate. Nevertheless the metal may slowly react and dissolve (forming a salt and water, but *not* liberating hydrogen), if *air* is bubbled through the acid, or if the acid has *strong oxidizing properties* (nitric acid and hot concentrated sulfuric acid, for example). If concentrated sulfuric acid or nitric acid is used the gas evolved is sulfur dioxide or one or more of the oxides of nitrogen.

5. Gold and platinum, at the very bottom of the list, react only with extremely vigorous oxidants such as aqua regia (a mixture of concentrated nitric acid with about 3 times its own volume of concentrated hydrochloric acid). (Ex. 15–20.)

89. Applying the Activity Series to Reactions of Reduction

If we attempt to reverse the reactions just considered, and *reconvert an oxide, hydroxide, or salt to metal,* we would expect that the activity series will apply in the reverse way. In other words, *reactions of reduction are most difficult when we are trying to reduce compounds of metals near the top of the series, and are relatively easy when we are trying to reduce compounds of metals near the bottom of the series.* More details:

1. Oxides or hydroxides or salts of *the most active metals* (those nearest the top of the series) can only be reduced by electrolysis or by heating them with a more active metal. For this reason these metals (the light metals) remained undiscovered until the beginning of the nineteenth century.

2. Oxides or salts of somewhat less active metals are reduced by being heated with carbon or aluminum:

$$3MnO_2 + 4Al \rightarrow 2Al_2O_3 + 3Mn$$

$$ZnO + C \rightarrow Zn + CO$$

3. Oxides and salts of *moderately* and *slightly active metals* are readily reduced to metal by being heated in a current of hydrogen or carbon monoxide:

$$CuO + H_2 \rightarrow Cu + H_2O$$

$$CuO + CO \rightarrow Cu + CO_2$$

4. Oxides and salts of the *least active metals* (the so-called noble metals) cannot be formed by direct oxidation. Once produced by

indirect means (for example with the aid of oxidizing acids), they are found to be unstable, readily decomposing on being heated:

$$Ag_2O \xrightarrow[\text{Heat}]{} 2Ag + \tfrac{1}{2}O_2$$

So it all makes a consistent picture: Metals near the top of the series react so readily that they are never found free in nature (except for meteoric iron). Their compounds are so stable that we ordinarily resort to electrolysis when we wish to decompose them. By contrast, metals near the bottom of the table are rarely found in nature except in the free condition. Their compounds are so unstable that even gentle heating will decompose them.

In short, *in descending the series, metals show a constantly* decreasing *tendency to enter the oxidized state and their oxides show a constantly* increasing *facility in being reduced to the metallic state.* (Ex. 21, 22.)

► 90. The Reaction of Metals with Acids as a Reversible Reaction

What has just been said implies that the reaction of a metal with an acid is sometimes reversible:

$$\text{Metal} + \begin{matrix}\text{Acid}\\ \text{or}\\ \text{water}\end{matrix} \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \begin{matrix}\text{Salt}\\ \text{or}\\ \text{metallic}\\ \text{hydroxide}\\ \text{(or oxide)}\end{matrix} + \text{Hydrogen}$$

Three cases are worth considering:

1. If the metal is a reasonably active one (*above iron* in the activity series) the forward reaction, liberating hydrogen, is *complete* and the reverse reaction (*b*) is practically excluded.

2. With moderately active metals and at least moderately active acids, the forward reaction may still predominate, but the reverse reaction (*b*) is detectible. The forward reaction (*a*) then remains incomplete. For example, when iron reacts with steam in a thick-walled bomb, it will not liberate hydrogen indefinitely, because a time comes in which hydrogen is liberated by the forward reaction (*a*) as rapidly as it disappears in the reverse reaction (*b*):

$$3Fe + 4H_2O \underset{(b)}{\overset{(a)}{\rightleftharpoons}} Fe_3O_4 + 4H_2$$

This is an example of chemical equilibrium (p. 62).

3. With very slightly active metals (those *below hydrogen* in the activity series) the forward reaction (*a*) is practically excluded, whereas

the reverse reaction (*b*) readily takes place. Thus metallic copper fails to displace hydrogen from steam or even from active acids. On the contrary, hydrogen, passed over heated cupric oxide, reduces it to metallic copper.

91. The Rate of Reaction of Metals with Acids

There is considerable practical interest in knowing something about the circumstances that determine the rate of reaction of metals with acids:

1. *Activity of the metal.* The more active of two metals will react the more rapidly with acids, if other factors are equally favorable. But the next few paragraphs will show that other factors are sometimes more important than activity.

2. *Activity of the acid.* Very slightly active acids, such as acetic or carbonic acid, react only very slowly, even with fairly active metals, like aluminum or zinc. This is not altogether due to the slight activity of the acid, but rather to the fact that *slightly active acids, when reacting with metals, usually produce slightly soluble salts.* These cover the surface of the metal with a closely adhering salt film, through which the acid cannot readily penetrate. The reaction therefore practically ceases.

3. *Concentration of the acid.* Ordinarily, the rate of reaction of a metal with an acid will increase with increasing *concentration of the acid* (the amount of acid present in unit volume of a solution). But when an acid is extremely concentrated, one is often surprised to note that the liberation of hydrogen often takes place very slowly or may actually cease. The reasons are not far to seek. Most salts are but slightly soluble in concentrated acids; and so, *when a concentrated acid is placed in contact with a metal, the reaction may produce a closely adherent film of salt or oxide, which is insoluble in the concentrated acid and prevents further action.* Furthermore, many concentrated acids are very *viscous;* because of this, the approach of acid molecules toward the surface of the metal and the movement of the reaction products away from the surface are very much slowed down. This, too, decreases the reaction rate.

4. *Temperature.* Increasing the temperature nearly always increases the rate of a chemical reaction. Moreover, metals that are completely resistant to all acids at room temperature are often rapidly corroded if the acids are heated. For example, metallic lead or iron, especially iron alloyed with a considerable proportion of silicon, will withstand the action of fairly concentrated, cold sulfuric acid; but

heating the acid makes it less viscous and increases its capacity for dissolving salts, and therefore enables it to attack metals that are immune to its action at ordinary temperatures.

5. *Purity of the metal.* Very pure metals or homogeneous *alloys* (mixtures or compounds of the metals with one another) often possess a surprising resistance to reaction with acids. This is important whenever we wish to protect a metal against the action of an acid. Iron or steel, for example, may be protected from corrosion by being given a continuous coating of very pure *zinc*, *lead*, *tin*, or even *aluminum*, in spite of the fact that these metals occupy positions well above hydrogen in the activity series.

On the contrary, particles of electrically conducting surface impurities (such as particles of carbon in ordinary zinc) often greatly increase the rate at which metals react with acids, for reasons to be explained in a later chapter (§ 516).

Any metal will react more rapidly with acids if it is placed in contact with another metal having a lower position in the activity series, or in contact with carbon. For this reason *non-homogeneous alloys* show very slight resistance to acids. (Ex. 23–25.)

92. Effect of Amalgamating a Metal

An alloy of another metal with mercury is called an *amalgam*. If zinc or aluminum, for example, is dipped in dilute acid to remove the nearly invisible film of oxide that is always present, we may amalgamate the surface by rubbing it with a droplet of metallic mercury, or by dipping it into a solution of a mercuric salt. The result is then surprising: zinc shows a greatly *decreased* but aluminum a greatly *increased* rate of reaction with acids.

FIG. 23. Growths of hydrous oxide on amalgamated aluminum.

The decreased rate of reaction, observed with amalgamated zinc, is due to an extra demand for energy, in liberating hydrogen at the surface of mercury (§ 521). But aluminum occupies a much higher position in the activity series than zinc. Amalgamating its surface loosens and breaks down the coating of oxide that ordinarily protects the metal from the attack of weak acids or moisture. The rate of reaction with acids or moisture is thereby increased.

Freshly amalgamated aluminum, when moistened, often liberates hydrogen so rapidly that it gets hot; if merely exposed to moist air it becomes covered with fantastic growths of hydrous aluminum oxide, within a few hours. This makes an interesting lecture experiment (Fig. 23). The mercury in the amalgam does not react and dissolve, for it is much less active than zinc or aluminum (*i.e.*, occupies a position much nearer the bottom of the activity series).

93. Properties of Hydrogen

1. *Physical properties.* Most conspicuous of the physical properties of hydrogen is its *lightness* (illustrated with soap bubbles or toy balloons). It is less than a fourteenth as heavy as an equal volume of air, and only a sixteenth as heavy as an equal volume of oxygen.

The fact just stated can readily be deduced from Avogadro's Principle. Equal volumes of hydrogen, air, and oxygen contain very nearly the same number of molecules. So the weights of equal volumes of these three gases must be in the same ratio as the weights of their individual molecules, namely 2 (for H_2), 29 (the average molecular weight of the gases composing the air), and 32 (for O_2). (Ex. 26–28.)

Hydrogen is *colorless*, *odorless* (when pure), *very slightly soluble in water*, and, *next to helium, the most difficult of all gases to liquefy* (compare data in Appendix D).

2. *Chemical properties.* When hydrogen is unmixed with oxygen it burns quietly in air or oxygen, with a nearly colorless flame, to produce water vapor:

$$2H_2 + O_2 \rightarrow 2H_2O$$

On the contrary, hydrogen mixed with even a few per cent of oxygen or air *explodes violently* on being ignited by a flame or spark. So be sure never to light or even strongly heat hydrogen that is being generated in the laboratory, until suitable tests (described by the instructor or in the laboratory manual) have assured you that it is free from air and is therefore safe.

A mixture of *hydrogen* and *chlorine* gases is safe as long as it is kept in the dark. But when exposed to bright sunlight or to the light of a burning magnesium ribbon, the two gases combine with a violent explosion, forming hydrogen chloride gas:

$$H_2 + Cl_2 \rightarrow 2HCl$$

Hydrogen combines readily with metallic sodium and several other metals, forming *hydrides* (NaH, CaH_2, etc.). As a lecture experiment

a small fragment of sodium may be heated in hydrogen in a porcelain boat. The product looks like common salt and even has the same crystal structure. But it reacts violently with water, liberating hydrogen.

Hydrogen is an important reductant. When oxides of the heavy metals (iron, copper, lead, etc.) are heated in a current of hydrogen they are reduced to *metal.* An interesting lecture experiment is the reduction of cupric oxide (black copper oxide) to bright metallic copper by heating the oxide in a current of hydrogen:

$$\underset{\text{Cupric oxide}}{CuO} + H_2 \rightarrow \underset{\text{Copper}}{Cu} + H_2O$$

(Ex. 29–31.)

94. Chemical Uses of Hydrogen

The chief uses of hydrogen in the chemical industries are:

1. As a *reductant* (reducing agent), reacting with metallic oxides at high temperatures, reducing them to metal. Hydrogen, or a mixture of hydrogen and nitrogen, is used to furnish a reducing atmosphere within furnaces for annealing or deoxidizing brass and other metals.

2. In producing *methanol* (formerly called "wood alcohol") and *formaldehyde.* In both these processes hydrogen is made to combine directly with carbon monoxide, in the presence of a catalyst:

$$CO + 2H_2 \rightarrow \underset{\text{Methanol}}{CH_3OH}$$

$$CO + H_2 \rightarrow \underset{\text{Formaldehyde}}{HCHO}$$

We here observe how the same reactants often give different reaction products, according to the catalyst used, and other conditions. (Ex. 32–34.)

3. In producing *ammonia,* by the direct union of hydrogen and nitrogen, under high pressures, in the presence of a catalyst:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

This process is discussed more fully in § 366.

4. In producing *gasoline substitutes,* by treating coal or petroleum with hydrogen, at moderate temperatures, under very high pressures, in the presence of catalysts.

5. In producing *hydrogenated fats and oils.* Many vegetable and animal fats and oils (cottonseed oil, or coconut oil, for example) may be made to combine with hydrogen gas in the presence of a catalyst (usually finely divided nickel), to form solid or semi-solid fats. Most of the lard substitutes now on the market are made in this way. Fish oils are also often hardened and deodorized by hydrogenation, as a first step in the preparation of soap.

For the preparation of ammonia, hydrogen is usually obtained from water gas (§ 87). Sometimes hydrogen is made by the reaction of iron with steam or by the electrolysis of water.

95. Use of Hydrogen in Welding

The oxyhydrogen flame is often used as a substitute for oxyacetylene, for welding alloys that might be injured by absorbing carbon from acetylene. In welding by *atomic hydrogen* an electric arc is struck (Fig. 24) in an atmosphere of hydrogen. At the high temperature of the arc, ordinary hydrogen molecules are to a large extent decomposed into molecules containing but a single atom (*atomic* or *monatomic* hydrogen):

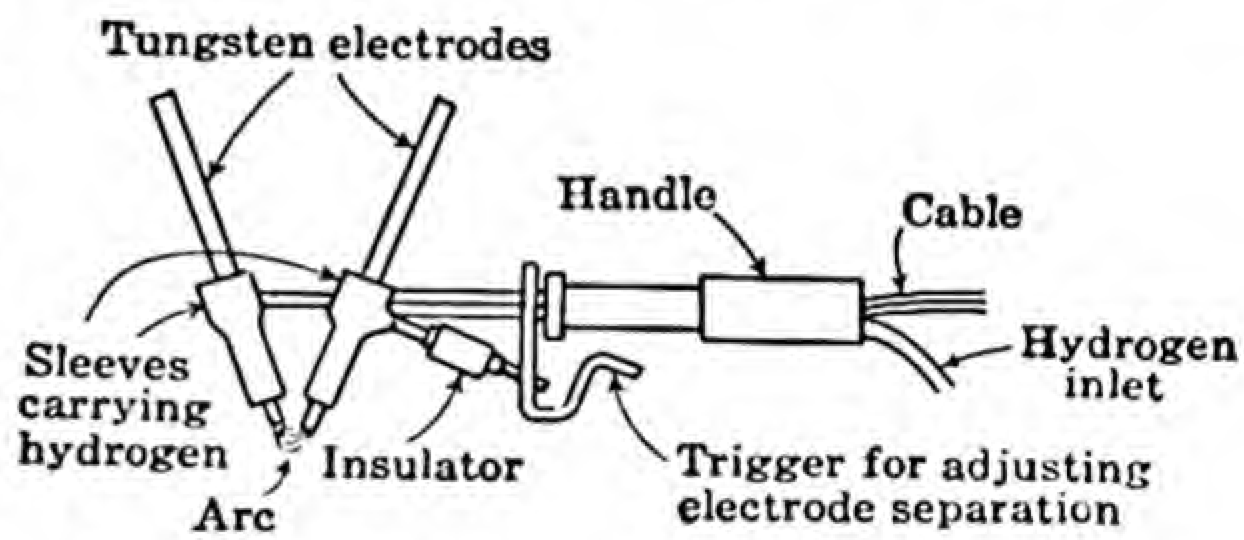


FIG. 24. Welding with atomic hydrogen.

$$H_2 + 76{,}000 \text{ cal} \underset{(b)}{\overset{(a)}{\rightleftharpoons}} 2H$$

A large quantity of heat disappears in the left-to-right reaction (*a*) —76,000 calories for every 2 grams of hydrogen (H_2); but as soon as the atomic hydrogen (H) has passed a short distance beyond the arc, the atoms recombine to form ordinary diatomic hydrogen, in the reverse reaction (*b*). In this way the heat that previously disappeared is once more released, and is *added to* the heat that is liberated by the burning of hydrogen in the zone of flame that surrounds the arc. An intensely hot zone is created at the welding tip, which reaches much higher temperatures than those created by burning ordinary hydrogen in oxygen.

96. Isotopes of Hydrogen

In 1932 it was discovered that about 1 atom in 5000, in samples of elementary hydrogen or compounds of hydrogen, possesses the relative

mass 2. This heavy isotope of hydrogen has been named *deuterium* and is represented by the symbol D or ^2H.

In 1934 a third isotope of hydrogen, of relative weight 3, was discovered. This has been called *tritium* (^3H). It is present in ordinary hydrogen and hydrogen compounds in the proportion of about 1 atom in more than 1,000,000,000.

The ordinary, light isotope of hydrogen, relative weight 1, is now often called *protium.*

When water is electrolyzed, the molecules that are composed of the more abundant isotopes of hydrogen and oxygen are decomposed somewhat more readily than those containing the less abundant isotopes. Consequently, a residue of water is left that contains an increased proportion of the heavy isotopes. By a systematic procedure, designed to save and return deuterium that would otherwise be lost in the later stages of electrolysis, a residue of nearly pure deuterium oxide, D_2O, has been obtained. This is "heavy water." It differs perceptibly from ordinary water in its physical properties and is slightly less active chemically:

	D_2O	H_2O
Freezing point	3.8°C	0°C
Boiling point (760 mm)	101.42°C	100°C
Vapor pressure at 25°C	15.2 mm	17.5 mm
Density at 20°C	1.1056	0.9982
Maximum density	1.1073 at 11.6°C	1.000 at 4°C

97. Conclusion

This chapter has furnished its fair proportion of questions still to be answered. Why do different metals differ so greatly in chemical activity? Why is a pure and homogeneous metal less active in displacing hydrogen than an impure sample of the same element? Why do surface impurities cause a metal to react more rapidly with acids than would otherwise be possible? What causes certain alloys to be acid-resistant? Why are catalysts necessary in most of the reactions in which hydrogen is applied in industry? Why are some chemical reactions readily reversible, whereas others are not?

These questions will have to await their turn in what follows. We must interweave a description of elements, compounds, and reactions with a discussion of general principles, seeking gradually to make the reader familiar with a large number of chemical facts, to serve as a background for the interpretation of facts that is our chief concern.

Technical Words

Inert, p. 87. **Cracking process,** p. 88. **By-products,** p. 87.
Salt, p. 89. **Hydroxyl group,** p. 91. **Alkali,** p. 91.
Activity series, p. 92. **Aqua regia,** p. 93. **Alloy,** p. 96.
Amalgam, p. 96. **Atomic or monatomic hydrogen,** p. 99. **Deuterium,** p. 100.

Stable—not readily decomposed; more precisely, having no tendency to decompose *spontaneously*.

Complete reaction—a reaction that proceeds in an indicated direction until one or more of the original reactants have been completely transformed.

Reversible reaction—a reaction which under proper conditions may progress in a given sense, or in the reverse sense, or in both these directions at once.

Active (or reactive)—tending to enter into a chemical reaction.

Reducing agent or reductant—in the narrowest sense, any substance capable of withdrawing oxygen from something else. (A broader definition in § 255.)

Hydrogenation—direct union with hydrogen, usually accomplished with the aid of a catalyst.

Hydrogenated—produced by direct union with hydrogen.

Concentrated—containing a relatively large amount of dissolved material in *unit volume* (1 ml or 1 liter).

Summary

§ 83. Relative abundance of uncombined or elementary hydrogen in the earth's atmosphere and in the solar atmosphere.

Names of some important materials or compounds containing hydrogen in combination with oxygen, nitrogen, carbon, carbon and oxygen, non-metals, metals.

§ 84. Two important simple compounds that may readily be decomposed, yielding hydrogen. An important industrial material that yields hydrogen as a by-product when it is decomposed.

§ 85. A rule that enables one to determine the relative volumes of gases or vapors concerned in a chemical reaction. Name given this rule when it is stated as a law.

§ 86. Two general methods for the preparation of any element.

What class of elements displace hydrogen from water and acids.

Equations for two reactions that produce hydrogen and a salt.

§ 87. Equation for the reaction of two light metals with water. Name of the product other than hydrogen that is obtained in each case.

Name given to soluble substances that turn red litmus blue.

§ 88. Three different names given to a list of the metals in the order of decreasing chemical activity.

Use of the series to predict the rate of reaction of metals with acids, for metals in different parts of the series.

§ 89. Application of the series in predicting the stability of metallic oxides and salts.

§ 90. Under what circumstances the reaction of a metal with an acid or water proves to be (1) complete and irreversible; (2) reversible; (3) impossible, the reverse reaction being complete.

§ 91. Five conditions that chiefly determine the rate of reaction of acids with metals.

Two acids that rate as slightly active. What other reason than slight activity is responsible for the slow rate of reaction of these acids with metals.

Two reasons why concentrated acids sometimes react very slowly with metals. Whether pure and homogeneous metals tend to react slowly or rapidly with acids. The effect of electrically conducting impurities on the rate of reaction of metals with acids.

§ 92. Name given to an alloy of another metal with mercury. How zinc or aluminum may be given a coating of this sort. Effect of such a coating on the rate of reaction of these metals with acids.

§ 93. Chief physical properties of hydrogen. Four different reactions to illustrate the chemical properties of hydrogen.

§ 94. Three or four different substances that are produced commercially by the direct union of hydrogen with other substances. Equations to illustrate.

An example of the use of hydrogen as a reductant.

What useful practical result is obtained by hydrogenating vegetable or animal oils.

Several important industrial sources of hydrogen.

§ 95. How atomic hydrogen is produced, and why it gives a higher temperature than is attained in the combustion of ordinary hydrogen, even in pure oxygen.

§ 96. Name given to variants of an element that differ in atomic mass. Names given to the two chief variants of hydrogen. What is meant by heavy water. How it is obtained.

Exercises

Review §§ 49, 50 before beginning these exercises.

1. From the balanced equation for the preparation of hydrogen by decomposing ammonia, determine how many molecules of ammonia are decomposed and how many of hydrogen are produced for each molecule of nitrogen produced. How many weight units of each gas appear in the balanced equation?

2. Write and balance an equation for the production of hydrogen by the electrolysis of water. How many molecules of hydrogen and how many of oxygen are produced from each molecule of water decomposed? How many weight units of each substance appear in the balanced equation?

3. What is a hydrocarbon? Ethylene, C_2H_4, contains what percentage of hydrogen, by weight?

4. What volume of pure oxygen, also what volume of air (21 per cent oxygen, by volume) is needed to burn 1000 cu ft of methane? 200, 952

5. Write and balance an equation for the complete combustion of ethylene, C_2H_4. What volume of oxygen is needed to burn 1 liter of ethylene gas, and what volume of carbon dioxide is produced? 300, 200

6. In the direct union of hydrogen and nitrogen gases, to produce ammonia, what volume of each reactant is needed for each 1000 cu ft of ammonia produced? 500, 150

7. Equal volumes of hydrogen are displaced from an acid when *equal numbers of atoms* of two specified metals react with the acid. If equal *weights* of these metals are used, will more hydrogen be liberated by the metal of the lower or by the one of the higher atomic weight?

8. Write and balance an equation for the action of magnesium on acetic acid, $HC_2H_3O_2$, one of the products being magnesium acetate, $Mg(C_2H_3O_2)_2$.

9. Write and balance an equation for the action of aluminum on sulfuric acid, H_2SO_4, one of the products being aluminum sulfate, $Al_2(SO_4)_3$.

10. Write and balance an equation for the reaction of potassium with water, one of the products being potassium hydroxide, KOH. How many atoms of potassium must be used for each molecule of hydrogen produced? How many weight units of potassium for each weight unit of hydrogen?

11. When sodium reacts with water, what weight of sodium must be taken for every 40 grams of sodium hydroxide, NaOH, produced? What weight of hydrogen will be produced at the same time?

12. Write an equation for the reaction of magnesium with steam, one of the products being magnesium hydroxide, $Mg(OH)_2$. What weight of magnesium is needed for each 10 grams of hydrogen produced?

13. Assuming that aluminum reacts with water to form aluminum hydroxide, $Al(OH)_3$, and hydrogen, write and balance an equation. What weight of aluminum is needed to set free 6 grams of hydrogen?

14. Write and balance an equation for the reaction of steam with iron. What weight of iron is needed for each 8 grams of hydrogen produced?

15. Write an equation to show that hydrochloric acid, HCl, reacts with metallic sodium to form common salt and hydrogen. How many grams of salt are produced from each 23 grams of sodium?

16. Write an equation for the reaction of potassium with acetic acid, $HC_2H_3O_2$, one product being potassium acetate $KC_2H_3O_2$.

17. Write an equation for the reaction of lead with hydrochloric acid, HCl, one product of the reaction being lead chloride, $PbCl_2$

18. Write an equation for the reaction of hot, concentrated sulfuric acid with copper, the products being cupric sulfate, $CuSO_4$; sulfur dioxide gas, SO_2; and water.

19. Which of the following metals would you expect to resist the action of dilute hydrochloric acid and dilute nitric acid, respectively: Cu, Pb, Cr, Pt, Sb?

20. Gold and silver are sometimes separated from an alloy of these two metals by heating the finely divided alloy with concentrated sulfuric acid. Which metal dissolves? By analogy with Exercise 18, what products should be obtained?

21. Write an equation for the reduction of ferric oxide, Fe_2O_3, to metal by reaction with metallic aluminum, which is oxidized to aluminum oxide, Al_2O_3. What weight of aluminum is needed for every 160 grams of ferric oxide? 540

22. Write an equation for the reduction of magnetic iron oxide to iron, the reductant being carbon monoxide. How does the volume of the gaseous product of this reaction compare with that of the carbon monoxide used?

23. Brass is an alloy of zinc and copper. Which of these metals reacts with acids, leaving the other metal almost unattacked?

24. Explain why galvanized (*i.e.*, zinc-covered) iron eaves troughs are never permitted to rest directly on copper brackets.

25. Why do tin cans (*i.e.*, tin-coated iron), if the tin-coating is incomplete or discontinuous, often corrode more rapidly than uncoated iron?

26. The molecular weight of hydrogen, H_2, is what fraction of that of helium, He (a *monatomic* gas)? What conclusion may we draw about the relative densities of these two gases? 500

27. Calculate the average molecular weight of a mixture of equal volumes (and hence equal numbers of molecules) of hydrogen and ethylene, C_2H_4. Roughly, how does the density of such a mixture compare with that of air? 150, 520

28. Which is the denser, air or a mixture of equal volumes of carbon dioxide and hydrogen?

29. What volume of air (21 per cent oxygen, by volume) is needed to burn a cubic foot of hydrogen? 238

30. In the direct union of hydrogen and chlorine gases, how does the volume of each reactant compare with that of the hydrogen chloride gas produced? 500

31. Write an equation for the reduction of cupric oxide by hydrogen. What weight of water is produced for each 79.5 mg of cupric oxide reduced? 180

32. What percentage by weight of hydrogen is contained in methanol? 125

33. Write and balance an equation for the reaction of calcium hydride, CaH_2, with water, the products being the same as in the reaction of calcium with water (§ 87). What weight of calcium hydride is needed to produce 1 kg of hydrogen by this method? 105

34. Write and balance an equation for the complete combustion of methanol. What volume of oxygen is needed for each liter of methanol vapor? 150

Chapter 8

THE PROPERTIES OF GASES

98. Gases Compared with Liquids

Gases, vapors, and liquids are often termed **fluids**—a word which indicates that such materials *flow*, and have no definite shape, other than that of the vessel that contains them. Important distinctions:

1. *Gases (including vapors) expand indefinitely, as opportunity is offered them*, hence completely fill a containing vessel, and have no definite upper surface. (A *vapor* is a gas that may be condensed to a liquid by increasing the pressure upon it, without lowering the temperature.)

2. Gases exert a pressure, *equally distributed over all the walls of the containing vessel.* Liquids exert only such pressure as is due to their weight, this pressure increasing with increasing depth, and being greatest on the bottom of the vessel.

3. Under ordinary pressures, gases are much *lighter* than liquids, *i.e.*, have a much lower *density* (the weight of a unit volume; for example, the weight in grams of 1 cubic centimeter).

4. *Two different gases, placed in contact, intermingle freely;* whereas two liquids often remain in separate layers (for example, oil over water).

5. *Gases expand much more than liquids do, when heated, and are diminished much more by pressure.*

Ordinary air and certain other gases, which happen to be difficult to liquefy, may actually be denser than liquid water, when they are under high pressures, though still remaining truly gaseous. Careful inspection of such a highly compressed gas would fail to distinguish it from a liquid, were it not for a simple test: *Offer it more space.* If the fluid being tested expands indefinitely, continuing to fill all the space offered it, it is a gas. If it separates into two distinct portions (liquid and vapor), separated by a definite surface, the original fluid was a liquid.

6. *The pressure that a gas exerts increases with increasing temperature.*

99. Explanation of the Properties of Gases

The properties just mentioned, which distinguish gases from liquids, are easily explained:

Facts about Gases	*Explanation in Terms of Molecules*
1. A gas expands indefinitely as more space is offered to it. 2. A gas exerts a pressure on the walls of the containing vessel.	The molecules of a gas are in rapid motion.
3. Gases are of relatively low density. 4. Gases intermingle freely. 5. Gases are readily compressible.	The molecules of a gas are relatively far apart.
6. The pressure that a gas exerts increases with increasing temperature.	The molecules of a gas move more and more rapidly as the temperature is increased.

The assumptions here made about molecules are the basis of what is often called the *kinetic-molecular theory* (literally, the theory of *moving molecules*).

100. The Ideal Gas

When we were discussing temperature (§ 77) we said that a completely logical temperature scale would make temperature proportional to the *collision-transferable energy* possessed by an *average molecule*. Then we looked about for a substance having some easily observable property which would be proportional to temperatures on the logical scale. We found none. But the *volume of a gas* (under constant pressure) or its *pressure* (with volume held constant) was found to be very nearly proportional to temperatures on the logical scale; and gases under very low pressures were found to be better yet. So we began to think of an *ideal gas*, whose volume or pressure would be exactly proportional to temperature, and which would therefore be an *ideal thermometric substance*.

To be completely ideal, a gas would have to satisfy three requirements:

1. Its molecules would have to be incapable of absorbing energy by being strained or distorted.

2. Its molecules would have to be so far apart as to possess no appreciable attraction for one another.

3. Its molecules would have to be of negligibly small size, relative to the space between them.

Molecules *undeformable, far apart, negligibly small!* Here are characteristics of an ideal gas which have some interesting con-

sequences. The first two of them imply that *none of the heat energy possessed by an ideal gas is potential energy* (due to forces tending to restore the shape of a strained molecule or forces of attraction between neighboring molecules). The only heat energy possessed by an ideal gas is *kinetic energy* (the energy of motion of its individual molecules). This is exactly proportional to the temperature of the gas, on the absolute scale.

Monatomic gases obviously come closest to satisfying the first requirement, whereas gases under low pressure come closest to satisfying the other two.

► 101. Why Compressing a Gas Liberates Heat

Everyone who has inflated a tire with a hand-pump knows that compressing a gas liberates heat. The compression of a mixture of air and fuel vapor in a Diesel engine makes the mixture get so hot that it ignites, driving the piston outward, without any need for an ignition system or spark plugs.

If you ask why compressing a gas makes it get hot, you will commonly get the answer that in compressing it we are compelled to do work, in moving the piston against the opposition of the force exerted by the gas. Work done on anything really means energy put into it. In compressing a gas this added energy takes the form of heat energy, and so raises the temperature.

This is all true enough; but we get a clearer view of what really happens if we focus our mind's eye on individual particles at the surface of the piston. The surface atoms of the piston are not stationary, but swing to and fro, with an average energy of motion that is determined by the temperature. If the piston is being pushed forward, its atoms are all being given some extra motion *toward the gas*. Gas molecules, in consequence, rebound from the piston with *increased average energy;* in other words, the temperature of the gas is increased. (Ex. 1.)

102. The Law of Boyle

Robert Boyle, in 1662, observed that doubling the pressure on a confined sample of air compressed the air to almost exactly half of its original volume. Multiplying the pressure fourfold compressed the air to almost exactly one-fourth its original volume. (In every such experiment he of course waited until the heat liberated in compressing the air had been dissipated, thus restoring the original temperature, before he measured the new volume of the gas.)

Other gases were later shown to behave in almost the same manner as air. Slight differences in compressibility that do exist between one gas and another tend to disappear when the gases are observed under low pressures. So, for an ideal gas, what Boyle found to be nearly true of air would be found to hold exactly: *The volume of an ideal gas is inversely proportional to the pressure upon it, if the temperature is held constant* (*Law of Boyle*).[1]

Since the volume of an ideal gas decreases in the same proportion as the pressure increases, *the product of the pressure and volume of an ideal gas remains constant as long as the temperature is constant.* This may be regarded as an alternative statement of the Law of Boyle.

In Fig. 25, for example, we have a sample of gas which occupies *unit volume* (1 cu ft or 1 liter) under *unit pressure* (1 lb per in.^{2} or 1 atmosphere). The product of pressure and volume at that point (the extreme left of the curve in Fig. 25) is therefore 1. But notice that this product has the same value at every other point on the curve. For example, at the extreme right it is $5 \times 0.2 = 1$. (Ex. 2–5.)

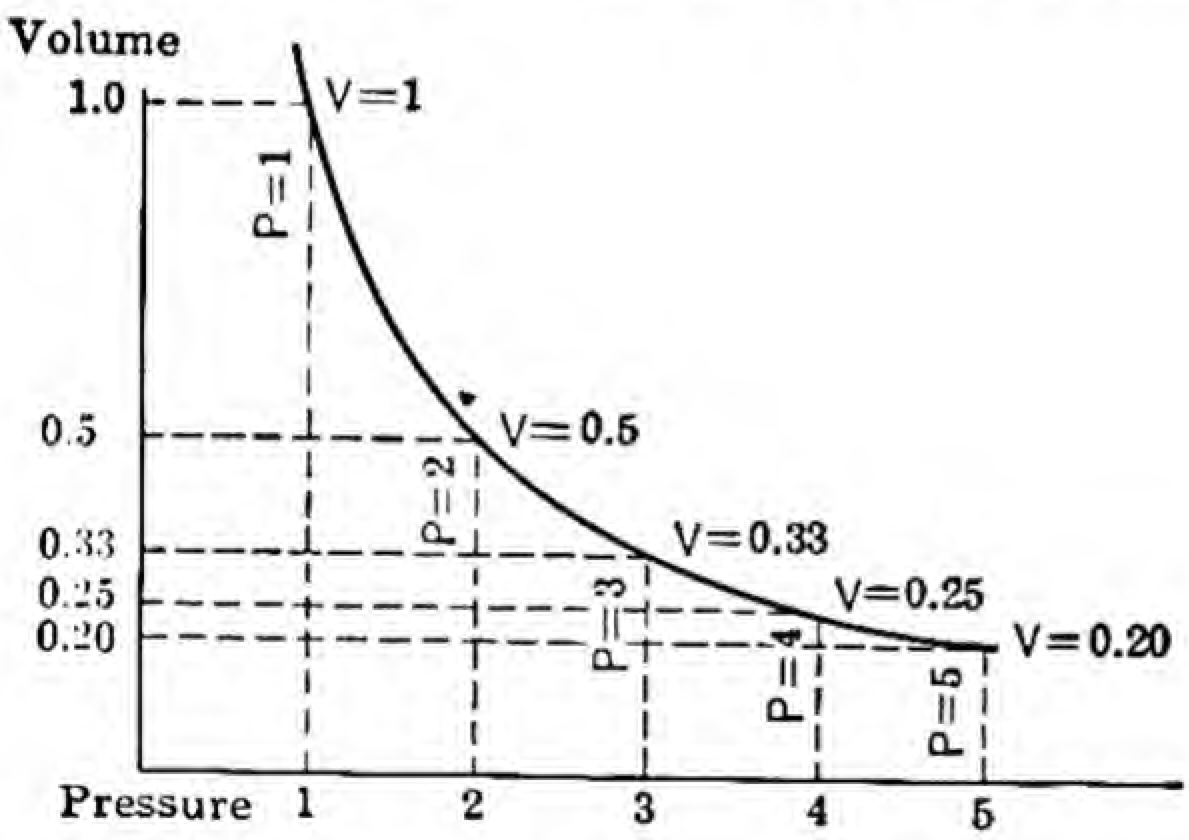


FIG. 25. The Law of Boyle.

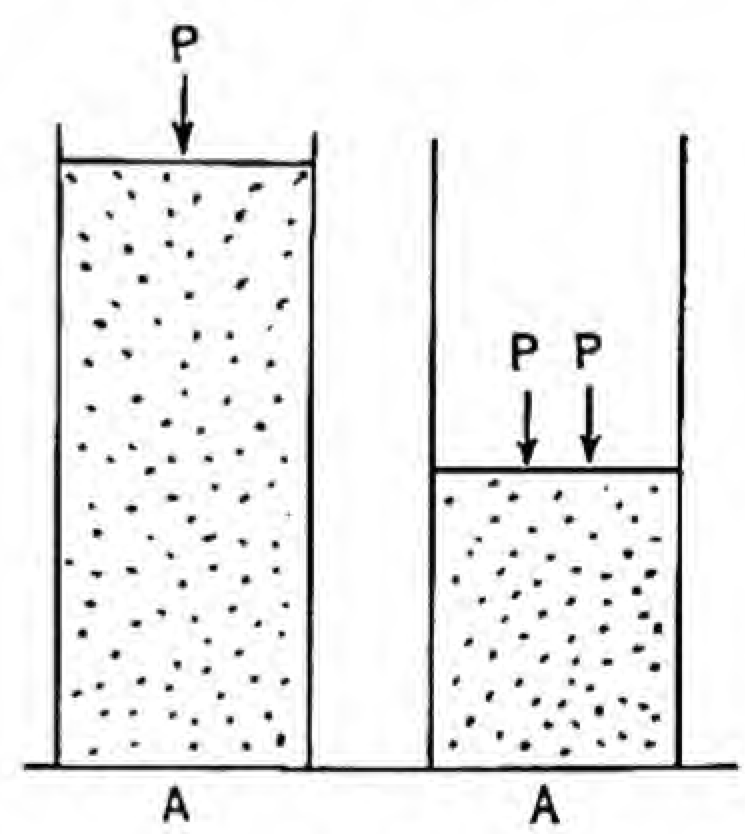


FIG. 26. The Law of Boyle explained.

103. The Law of Boyle Explained

To explain the Law of Boyle, consider a gas confined within a cylinder fitted with a movable, frictionless piston (Fig. 26). If the piston is at rest we know that the external pressure, P (directed inward, toward the gas), is balanced by an equal pressure, directed outward, and due to the gas molecules rebounding from the inner wall of the piston.

Now let the external pressure, P, be doubled. The piston will be driven inward, confining the gas within a smaller volume. If the tem-

[1] Inversely proportional means that as one quantity becomes larger the other becomes smaller, in the same proportion.

perature is kept constant, the molecules, on the average, will possess the same speed as before; but since the distance from piston to the opposite end of the cylinder, at *A*, is now less than before, each molecule will return to the piston and rebound from it more frequently. As soon as the distance from the piston to the opposite wall, *A*, and hence the total *volume* of the gas, has been reduced to half what it was before, each molecule will rebound from the inner surface of the piston twice as frequently as before. The pressure exerted by the gas, directed outward, will consequently be doubled, and will balance the doubled external pressure, *P*, and bring the piston to rest. In brief, *doubled external pressure results in halved volume.*

104. The Law of Charles

When a gas or vapor is in a freely expansible container, such as a thin-walled rubber balloon or a cylinder fitted with a frictionless piston, an increase in the absolute temperature proportionately increases its *volume*. If the gas or vapor, on the contrary, is in a vessel with rigid walls, such as a stoppered bottle or steel cylinder, an increase in the absolute temperature proportionately increases *the pressure* that the gas exerts.

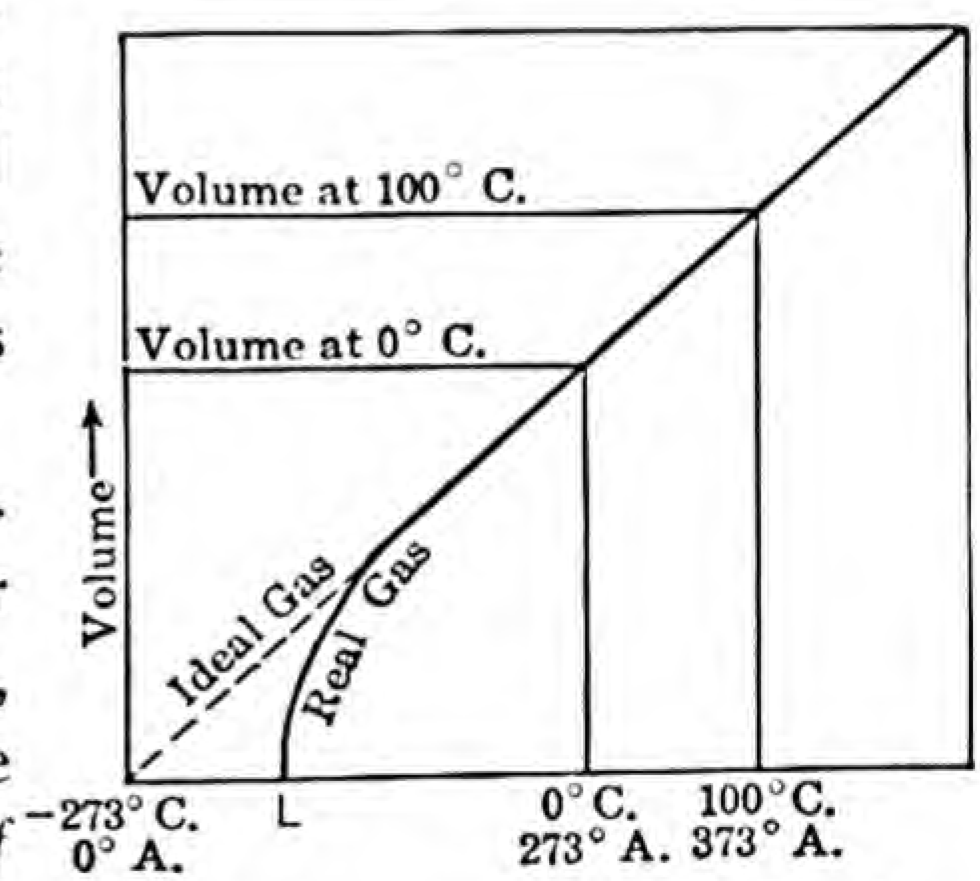


FIG. 27. The Law of Charles.

Air in a tire represents an intermediate case. Since the tire is neither freely expansible nor completely rigid, an increase in the absolute temperature proportionately increases *the product of pressure and volume.* If a truck tire, for example, becomes heated from 27°C (300°A) to 57°C (330°A), this 10 per cent increase in the absolute temperature causes a 10 per cent increase in the product of pressure and volume; but since the increase in *volume* is slight there will be almost a 10 per cent increase in the *pressure* exerted by the air within the tire. Such calculations of course assume that the confined air or gas is ideal.

The first of the three cases just discussed is that covered by the *Law of Charles*, as ordinarily stated: *The volume of an ideal gas, confined under a constant pressure, is very nearly proportional to the absolute temperature.*

Figure 27 shows the steady contraction of an ideal gas, as its temperature is lowered, until its volume finally shrinks to zero at

absolute zero. That this does not actually happen, with any real gas, need not cause any concern. There is, of course, no such thing as a completely ideal gas. Figure 27 shows that real gases, at sufficiently low temperatures, begin to shrink much more rapidly than an ideal gas, then liquefy (at L) and finally solidify. The liquid or solid thus produced has a volume that is nearly negligible in comparison with the original gas. (Ex. 6–8.)

► 105. The Law of Charles Explained

We may account for the Law of Charles in a very simple way if we consider a gas confined within a cylinder, fitted with a frictionless, movable piston (Fig. 28). If we double the absolute temperature of the gas, its molecules acquire twice their former average kinetic energy. Then the change in kinetic energy, in stopping any molecule and hurling it back, once, from the surface of the piston, will average twice what it was before; hence the force that the molecules exert, each rebounding once from the piston, will be twice what it was before.

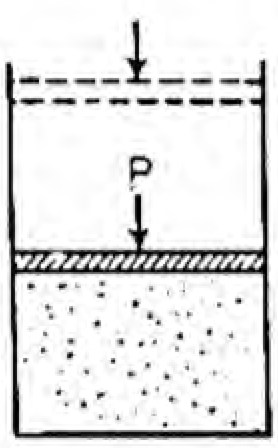


FIG. 28.

The doubled pressure will drive the piston outward until the volume has been doubled, so that the distance each molecule has to move between successive rebounds from the piston is twice what it was before. The doubled force of each tiny blow against the piston will then be just offset by the fact that these blows are delivered only half as frequently as they were before the piston moved. The piston will therefore cease to move, and doubled absolute temperature will have resulted in doubled volume.

106. Recalculating Gas Volumes

Gases that have been liquefied are usually sold in closed steel cylinders at so much a pound. But those delivered in gaseous form, through pipes laid to the doors of our homes and factories, are sold at so much a thousand cubic feet—a measure of *volume*. This practice introduces a difficulty, since the volume of a gas depends on the temperature and pressure. To avoid it, your gas bill ought to state what the volume of the gas sold you *would have been* if measured under what are called *standard conditions*. This means a temperature of 0°C or 32°F (the freezing point of water) and a pressure of *1 atmosphere* (76 cm or 760 mm or about 30 in. of mercury).

In determining what volume a gas will occupy under altered conditions of temperature and pressure it is best not to apply the laws of

Charles and Boyle in the form of a proportion, but to reason the problem out, according to the following model:

A gas occupies 25.45 ml at 20°C, under 740 mm pressure. Required: its volume at 0°C, under a pressure of 1 atmosphere (760 *mm*).

Original conditions:

$V_1 = 25.45$ ml $\quad T_1 = 273 + 20 = 293°$A

$P_1 = 740$ mm

Final conditions:

$V_2 = ?$ ml $\quad T_2 = 273 + 0 = 273°$A

$P_2 = 760$ mm $\quad$ Standard conditions

Be sure that all temperatures are converted to the absolute scale.

Notice, first, that the gas is *cooled* from 20°C to 0°C, or from 293°A to 273°A, pressure meanwhile remaining constant at 740 mm. It will plainly contract and occupy a smaller volume than before. The original volume must therefore be multiplied by a fraction smaller than 1, evidently $\frac{273}{293}$.

Next the pressure is increased from 740 to 760 mm. The gas is thereby compressed, and again occupies a smaller volume than before; the preceding volume must therefore be multiplied by another fraction smaller than 1, namely, $\frac{740}{760}$. For the final volume we have then:

$$V_2 = 25.45 \text{ ml} \times \frac{273}{293} \times \frac{740}{760} = 23.10 \text{ ml}$$

In brief, *multiply the original volume by two successive fractions, which are smaller or larger than one, according as the volume is seen to decrease or increase with the indicated changes in temperature and pressure.* The same method may still be used if the volumes are expressed in some other unit, for example in cubic feet, and the pressures in atmospheres or in pounds per square inch. (Ex. 9–16.)

107. Energy Stored Within a Compressed Gas

There is another method for dealing with such problems. We have stated (§ 104) that when a gas is stored in a tire or other container that is perhaps not completely rigid, an increase in the *absolute temperature* proportionately increases *the product of pressure and volume.* But if this product increases or decreases in the same proportion as the absolute temperature, then the ratio, PV/T(abs), must remain constant for any given sample of the gas, in spite of changes in the three quantities concerned. Let these three quantities, under the

original conditions, be indicated by the subscript 1, and under the final conditions by the subscript 2. Then, because PV/T must remain constant, we may write:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Any one of the six quantities in this equation can be found from the equation if the other five are given. Be sure that temperatures are converted to the absolute scale.

We mentioned this method, not because it is any shorter or more valuable than the other, but because it reveals a principle which should prove useful to anyone who may ever have to deal with gases stored in tanks or tires. The *product of pressure and volume, PV,* is really a measure of the *energy* that is stored within the compressed gas. It is this stored energy which is doubled when we double the absolute temperature of a gas. This is because doubling absolute temperature doubles the total energy of motion of the molecules of the gas.

So a large truck tire, carrying air under 70 lb (per sq in.) pressure, is much more than twice as dangerous as a smaller auto tire under 35 lb (per sq in.) pressure. In each instance you must multiply the pressure by the volume (say 5000 cu in. for the truck tire and 1000 cu in. for the auto tire) to get the total energy stored in the tire. Then

$$PV \text{ (truck)} = 70 \frac{\text{lb}}{\text{in.}^2} \times 5000 \text{ in.}^3 = 350{,}000 \text{ in.-lb}$$

$$PV \text{ (auto)} = 35 \frac{\text{lb}}{\text{in.}^2} \times 1000 \text{ in.}^3 = 35{,}000 \text{ in.-lb}$$

In other words, the energy stored in the truck tire is 10 times that stored in the auto tire. That has to be taken into account in designing the truck tire. If it blows out, beware! It stores enough energy to rip through heavy fabric and do plenty of damage.

Our calculation incidentally shows that

$$\frac{\text{lb}}{\text{in.}^2} \times \text{in.}^3 = \text{in.-lb}$$

Treating the symbols of the units as if they were ordinary symbols of algebra, we see that the result must be inch-pounds, which is a measure of energy. This example will serve as an introduction to

dimensions, a useful aid to numerical clear thinking, discussed in Appendix H.

Further to emphasize PV as a measure of stored energy, consider a transport plane, coming in for a landing. The kinetic energy of the vertical part of its motion must all be absorbed in the springs and tires of its landing gear. The springs and the tire walls of course absorb part of this energy, in being deformed. But most of it must be absorbed by the air in the tires.

So the air in the tires must have a considerable capacity for storing energy; in other words, it must be capable of a considerable increase in PV. If this is to take place without too great an increase in pressure then the volume must be large. Thus we account for the overstuffed appearance of an airliner's tires. They are of very special design, which attains low *pressure* by going all out for *volume!*

The energy absorbed in landing gear and tires is there liberated as *heat;* but when this has been conducted away and the original temperature restored, the confined air has the same PV, hence the same energy content as before, even though it is now compressed into a smaller volume by the weight of the plane.

Finally, consider air being pumped into the ballast tanks of a submarine. The product, PV, of the pressure under which air is introduced into them and their total volume represents energy or work. It is the total work that must be performed to empty the tanks of water and so bring the submarine to the surface.

108. Departure of Real Gases from Ideal Behavior

The molecular theory explains the chief properties of an ideal gas, in complete agreement with precisely stated laws (§§ 102, 103). Yet an afterthought must diminish our sense of satisfaction. We find it easy to account for the properties of an ideal gas—but no such gas exists! An ideal gas is merely a limit toward which real gases approach when observed under lower and lower pressures.

With real gases we find the following departures from ideal behavior:

1. *At high temperatures* real gases are somewhat *less* compressible than an ideal gas, as shown by the curve A, in Fig. 29, next page.

2. As the temperature is lowered this departure from ideal behavior is gradually diminished and finally reversed. So, *at moderate or low temperatures* (if the pressure is not too great), real gases are somewhat *more* compressible than an ideal gas, as shown by the curve B in Fig. 29

This extra compressibility is most conspicuous for gases that are easiest to liquefy, and it may be regarded as *a tendency toward liquefaction*, which under higher pressures results in actual liquefaction. The only gases which fail to display extra compressibility at room temperature, as compared with an ideal gas, are hydrogen, helium, and neon—the very three that are hardest to liquefy.

3. *At sufficiently low temperatures all gases may be liquefied by sufficiently high pressures.* If the temperature is not sufficiently low to

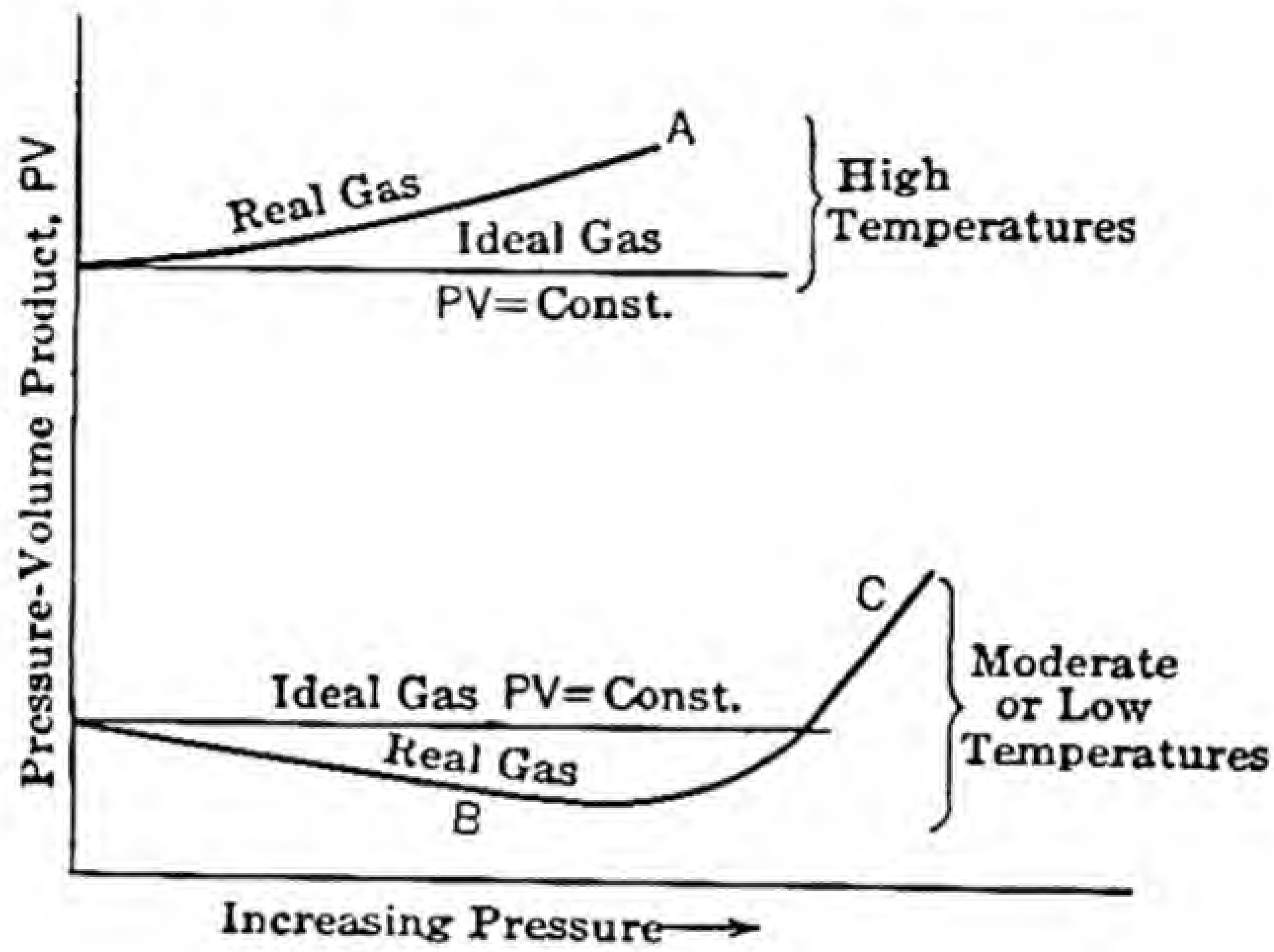


FIG. 29.

permit a gas to be liquefied by the application of pressure we find that the gas, under very high pressures, is always less compressible than an ideal gas, as shown by the curve C in Fig. 29.

By taking account of the deviation of any real gas from ideal behavior it is possible to determine its molecular weight much more accurately than is possible if one merely compares its density with that of oxygen, as described in § 32.

109. Explanation of the Facts Just Given

So much for the *facts* concerning the properties of real gases. We obviously have to do with two opposing tendencies. One takes command at high temperatures, making a real gas *less* compressible than an ideal gas; the other at low temperatures, under low or moderate pressures, making a real gas *more* compressible than an ideal gas.

Actually we did make two assumptions about an ideal gas which are not quite justified for real gases and which would have opposite effects:

1. *We assumed the molecules of a gas to be of negligible size, in comparison with the space between them.* Since their size is not entirely

negligible their movements bring them into collision with the walls more frequently than would happen if their size were negligible. The result is an extra pressure, directed outward. This amounts to *an extra resistance to compression*, which becomes more and more pronounced the greater the pressure, because, with increasing pressure, the volume of the molecules becomes a greater and greater fraction of the total volume. Thus we account for real gases being *less* compressible than an ideal gas, especially under high pressures, provided that the temperature is not too low.

2. *We assumed the molecules of a gas to be so far apart as not to attract one another.* Nevertheless, at low temperatures a gas shrinks to such a small volume that its molecules get close enough together to attract one another appreciably. This tends to make real gases, at sufficiently low temperatures, *more* compressible than an ideal gas.

The first effect, tending toward lessened compressibility, is still present at low temperatures, doubtless more than ever. But at low temperatures it is overshadowed by the second effect, tending toward increased compressibility.

At still lower temperatures the molecules approach so closely and attract one another so strongly that they no longer scatter indefinitely, filling the whole of the containing vessel, but are restrained within some definite volume—in other words, form a *liquid*, with a definite upper surface.

110. Accounting for Avogadro's Principle

Avogadro's Principle (§ 31) is a necessary consequence of our ideas concerning molecules. Consider two identical vessels (Fig. 30) filled with two different gases, at the same temperature, T, and under the same pressure, P. Since both gases are at the same *temperature* both have the same *average energy of straight-line motion, per molecule*. Since both exert the same *pressure* against the walls of the two vessels, it is evident that the *total change in kinetic energy*, all the molecules being first brought to a stop, then rebounding from any wall, is the same for one gas as for the other.

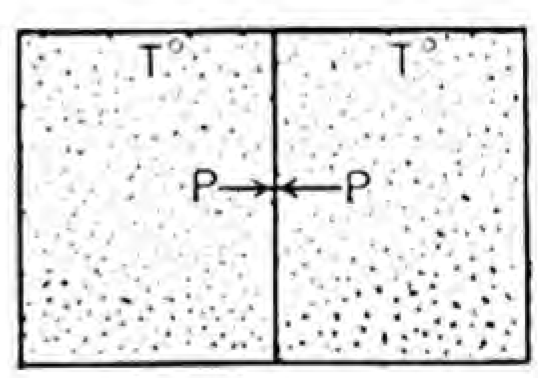


FIG. 30.

Equal average kinetic energy per molecule and equal total energy for all the molecules! This evidently is possible only if we have *equal numbers of molecules*, in the equal volumes considered. By analogy, if two communities possess equal per capita wealth and equal total wealth they must have the same population.

We justify Avogadro's Principle in another way if we recall (§ 73) that all molecules, whether heavy or light, at any given temperature, possess the same per-molecule average kinetic energy of straight-line motion, $\frac{1}{2}mv^2$. Light molecules therefore make up in velocity-squared for what they lack in mass, and so beat back their neighbors on all sides to the same average distance as they would if they were heavy. Thus a given volume of an ideal gas or vapor contains a definite number of molecules, regardless of their mass or chemical nature. This is not true of liquids or solids, and is only approximately true of real gases. (Ex. 17.)

111. Diffusion. The Law of Graham

When a bottle of perfume is opened its odor can soon be detected in distant parts of a room, even when the intervening air is at rest. The obvious explanation is that the molecules of the perfume vapor are in rapid motion and readily penetrate between and become scattered among the molecules of air. Their collisions with the molecules of air frequently deflect them from their course and occasionally turn them back, so that they follow a zigzag path and require some time to go even a few yards. In a vacuum their flight would be uninterrupted, and they would traverse distances of perhaps a hundred yards within a second.

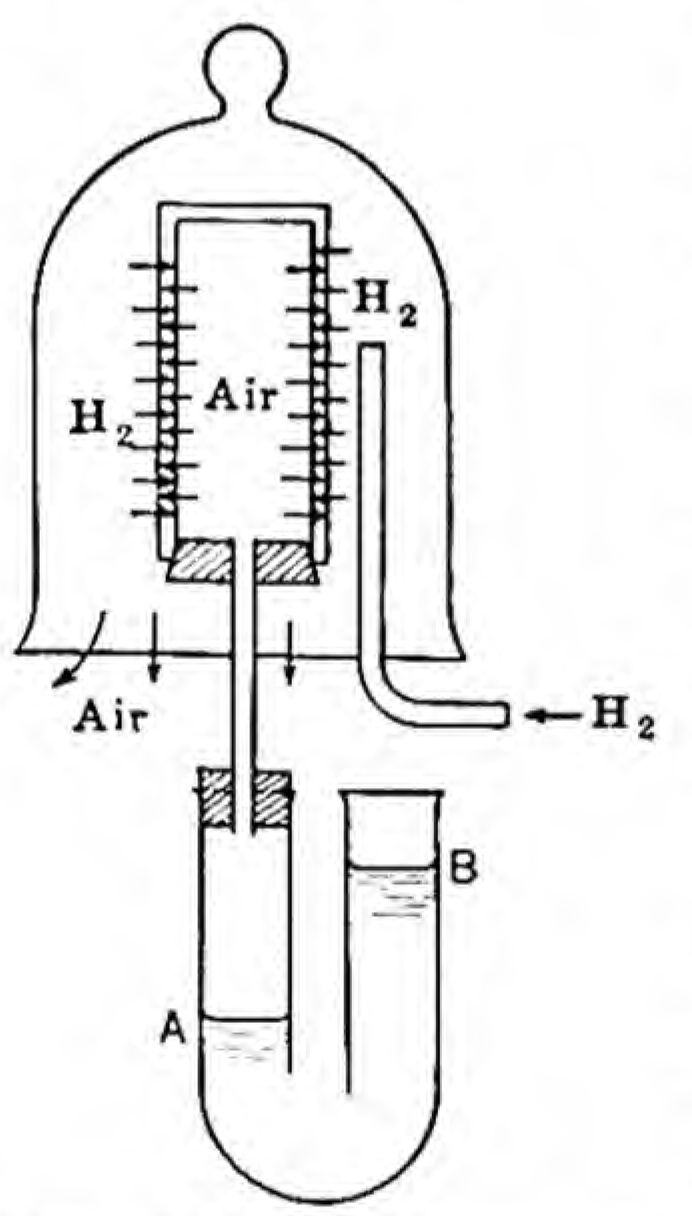


Fig. 31. Diffusion of hydrogen.

Such a spontaneous intermingling of the molecules of two substances is termed *diffusion.* When two gases are separated by a porous wall (one containing a multitude of microscopic openings) their intermingling by diffusion is very much slower than it would be if the wall were absent; but it nevertheless takes place, at a rate which must evidently depend on the number and size of the openings in the wall, on the number of molecules of each gas in a unit volume, and on their average speeds.

Light gases diffuse more rapidly than heavy ones. This may readily be demonstrated as a lecture experiment (Fig. 31). Hydrogen gas is passed into the space between a porous pipe-clay cylinder and the surrounding bell-jar. Since hydrogen is very much lighter than air it diffuses inward through the pores of the cylinder much more rapidly than the air within can diffuse outward. Thus a pressure is set up

within the cylinder, which depresses the liquid in one arm, A, of a large U-tube. After a considerable amount of hydrogen has passed into the cylinder, the bell-jar is removed. Hydrogen within the cylinder then passes out through the porous walls more rapidly than air can pass in, hence the liquid in the U-tube will rise at A and fall at B.

For any specified temperature and pressure, the volume of gas diffusing through a porous wall in a specified time is inversely proportional to the square root of the molecular weight or density. This is the *Law of Graham* (1829).

Observe that *this law compares the volume rates of diffusion of different gases, under the same conditions*, not those of one and the same gas under different conditions. Thus, the density or molecular weight of sulfur dioxide gas is 16 times that of helium. Sulfur dioxide therefore diffuses the more slowly, in fact, $\sqrt{16} = 4$ times as slowly as helium. If a porous wall passes 100 ml of helium in a given length of time, it will pass only 25 ml of sulfur dioxide. (Ex. 18–23.)

Diffusion in liquids takes place much more slowly than in gases; nevertheless a particle of a soluble colored substance, layered over with water in a deep cylinder, will dissolve, wander upward by diffusion, and after a few weeks will color the whole liquid. Even solids, placed in contact, sometimes slowly mingle by diffusion. Gold from a gold plate, clamped against a block of lead, will mingle with the lead in detectible amounts in the course of a few years.

112. Accounting for the Law of Graham

The rate at which a gas diffuses through a porous wall does not depend on the *size* of its molecules. The openings in a porous wall are often microscopically visible, and are therefore so large that the molecules have no difficulty at all in passing through. But the more molecules we have on one side of a porous wall and the more rapidly they move the more of them will happen to encounter openings in the wall, during each moment of time, and pass through. In other words, the number of molecules diffusing through a porous wall, hence the *volume* of gas diffusing through it, is proportional to the *number of molecules* in unit volume and to their *average speed*.

To simplify the comparison, let us take two different gases under the same pressure and at the same temperature. Since conditions are the same, the number of molecules in unit volume is the same for both gases (Avogadro's Principle). Since both gases have the same *temperature*, the per-molecule average energy, $\frac{1}{2}mv^2$ (where m is the mass

and v the velocity corresponding to average energy), is also the same for both gases. So, *whatever the molecules of either gas lack in mass they make up in velocity squared.* In other words, v^2 is inversely proportional to m, and v itself is inversely proportional to the square root of m.

To summarize: When two gases are compared under identical conditions they both contain the same number of molecules in unit volume; but the average velocity of these molecules, hence the volume rate of diffusion of the gases, is inversely proportional to the square root of the molecular weight, hence inversely proportional to the square root of the density. This is Graham's Law.

113. Finding the Average Speed of Molecules

From the pressure that the gas exerts, at any given temperature, it is possible to calculate the average speed of its molecules, even without knowing how many molecules there are, for the simple reason that we do know their total mass, which is the mass of the gas sample as a whole. It turns out that molecules of hydrogen, the lightest known gas, have an average-energy velocity [2] at room temperature (namely, around 20°C) of about a mile a second.

Heavier molecules move more slowly. We have just shown that *the average-energy velocity of the molecules of a gas, at any given temperature, is inversely proportional to the square root of the density or molecular weight of the gas.* Thus oxygen gas, which is 16 times as heavy as the same volume of hydrogen, has molecules with an average velocity only $\sqrt{\frac{1}{16}} = \frac{1}{4}$ that of molecules of hydrogen. (Ex. 24, 25.)

It is easy to see that the molecules of a gas must constantly change their velocities as they collide with one another and with the walls of the containing vessel. Thus some of them come to have much higher and others much lower velocities than the average-energy velocity, which we have just calculated.

The British physicist Maxwell (1860) carried through a calculation that proved that about half of the molecules of a gas possess velocities that are within 30 per cent of the average-energy velocity, at any given temperature. About 1 molecule in 50,000 has more than 3 times, and about 1 in every 150,000,000 more than 4 times, the average-energy velocity. In the upper part of the earth's atmosphere, therefore, molecules occasionally acquire a sufficient velocity to escape entirely

[2] We have called this the average-energy velocity, since it is the velocity that gives to any molecule the average energy for all the molecules, at that temperature. It is not the same thing as the arithmetical average of the different velocities themselves.

from the earth's attraction. Fortunately for us, any such impulse on the part of an atmospheric molecule is usually thwarted by collisions with more slowly moving neighbors. Were this not true the earth, ere this, would have completely lost its atmosphere, as long ago happened to the moon, on account of its weaker gravitational attraction.

114. Estimating the Sizes of Molecules

Though molecules of all gases at ordinary temperatures travel several hundred yards a second, no molecule can travel very far before it collides with another and is turned back. Gases and vapors therefore tend to linger near the place where they are released. Were this not so we would not know that blossoms possess odor. Calculations show that the molecules of gases under ordinary atmospheric pressure have an average "free flight" or *mean free path* between successive collisions of less than a hundred thousandth of an inch. That means that an average molecule, traveling perhaps a quarter of a mile per second, experiences as many collisions in that time as a watch makes ticks in a human generation. Molecules must be of very substantial construction or they would long ago have been completely worn away by collision with one another since the universe came into being. *As the pressure upon a gas is reduced the mean free path of its molecules is proportionately lengthened.*

By forcing a gas through a very fine opening (a capillary tube) one may form an idea of the size of its molecules. This is *not* because any openings that are visible and measurable under a microscope are ever small enough to catch and hold back a molecule. A glimpse of what really happens is obtained if we consider a drove of animals being driven through a barnyard gate. If the animals are in a frolicsome mood their passage through the gate is sure to be retarded by their collisions with one another. The larger they are the more frequent their collisions, and the shorter their mean free path. Knowing their average speed and the width of the gate, one might make some estimate of their size from their retardation in passing through the gate. Thus calculated, molecules turn out to be so very small that a special unit is adopted for their measurement, the *Ångström unit* (Å), which is 10^{-8} cm or about $\frac{1}{250,000,000}$ of an inch. (The expression 10^{-8} means a 1 in the eighth decimal place, preceded by zeros. See Appendix E.)

Small as molecules are, we inhale so many with every breath of air we draw that if we placed them in contact, like pearls on a string, they would girdle the earth about one hundred thousand times.

Diameters of Molecules of Some Common Gases

(Expressed in Ångström units)

Hydrogen	2.4	Carbon dioxide	3.36
Helium	1.9	Oxygen	2.97
Ammonia	2.97	Nitrogen	3.15

Technical Words

Fluid, p. 105. **Vapor,** p. 105. **Standard conditions,** p. 110.
Diffusion, p. 116. **Mean free path,** p. 119.
Ångström unit (pronounced *Ông'strum*), p. 119.

Ideal gas—one whose molecules are without appreciable attraction for one another and of negligibly small size in comparison with the space between them.

Dimensions—an expression of the power or exponent to which certain fundamental units enter into the definition of a complex unit.

Summary

§§ 98, 99. List the most conspicuous properties of gases, and indicate what assumptions are made about molecules to account for each property.

§ 100. Indicate why the concept of an ideal or perfect gas was invented.

Under what conditions do real gases most nearly possess the properties of an imaginary ideal gas?

What kind of energy is possessed by an ideal gas?

§ 101. Explain why a gas, when very quickly compressed (for example, beneath the piston of an engine), is always much less compressible than it would be found to be if slowly compressed.

§§ 102, 103. With the aid of a diagram, explain why increasing the pressure on an ideal gas tenfold, temperature remaining unchanged, will compress the gas to one-tenth its former volume.

§ 104. Samples of a gas are contained respectively in freely expansible, rigid, and semi-rigid containers. Indicate what is proportional to the absolute temperature in each case. Which of the three is covered by the Law of Charles?

§ 105. With the aid of a diagram, explain why halving the absolute temperature of a gas confined under constant pressure will cause it to contract to half its original volume.

§ 106. Explain how one may calculate the volume which a sample of gas will occupy under altered conditions of temperature and pressure.

§ 107. How we may calculate the total energy stored in a compressed gas. Why this quantity is proportional to the absolute temperature.

§ 108. Are real gases more or less compressible than an ideal gas, (1) at high temperatures; (2) at moderate or low temperatures; (3) under high pressures?

§ 109. Show how two opposing tendencies explain the facts just referred to.

§ 110. With the aid of a diagram, demonstrate Avogadro's Principle.

§ 111. What is meant by diffusion? Describe and sketch an experiment to show that hydrogen diffuses more rapidly than ordinary air.

Mention examples of diffusion in liquids and solids.

§ 112. What two factors determine the rate of diffusion of a gas through any given porous wall? Then show that when two samples of gas have the same temperature and pressure their rates of diffusion will be as stated by Graham's Law.

§ 113. What is meant by the average-energy velocity of gas molecules? About what is this velocity for hydrogen molecules, at room temperature? For oxygen molecules?

What did Maxwell prove with regard to the velocity of gas molecules, at any given temperature?

§ 114. What name is given as a unit of length to the hundred millionth of a centimeter?

In round figures, about what is the diameter of the molecules of some common gases?

Exercises

1. On the model in the text (which shows why heat is liberated in compressing a gas), explain the opposite case; in other words, explain why a gas is cooled when it expands, driving a piston before it.

Would an ideal gas be cooled in expanding into a vacuum?

2. The volume of a gas is 20 cu ft at 0°C, under a pressure of 2 atmospheres. What volume will it occupy under standard conditions (0°C, under 1 atmosphere pressure)?

3. If we double the pressure on an ideal gas, temperature remaining unchanged, what do we do to its volume? Then what do we do to its density?

Is the density of an ideal gas therefore directly or inversely proportional to the pressure upon it, if the temperature remains unchanged?

4. What volume of gas under 1 atmosphere pressure will have the same weight as 1 liter of the same gas, under 5 atmospheres pressure, if both samples have the same temperature?

5. When we reduce the pressure on a gas to one-tenth its former value, what do we do to the volume and to the number of molecules in unit volume, temperature remaining unchanged? What do we do to the energy of an average molecule?

6. A gas occupies 12 liters at 27°C. What volume will it occupy at 127°C, under the same pressure? (*Hint:* Change the temperatures to the absolute scale; then apply the Law of Charles.) 160

7. What do we do to the volume of a gas and to the number of molecules in unit volume if we double the absolute temperature?

8. What is the weight of 1 liter of a gas at 200°A, if 1 liter weighs 2 grams at 400°A, under the same pressure?

9. A gas occupying 100 ml under standard conditions will occupy what volume at 273°C = 546°A, under a pressure of 5 atmospheres? (*Hint:* First find the new volume when the temperature changes, pressure remaining unchanged; then find the effect of increasing the pressure to 5 atmospheres.) 400

10. A gas occupying 200 ml at 27°C, under a pressure of 700 mm, will occupy what volume under standard conditions? (1 atmosphere = 760 mm.) 168

11. A gas that occupies 10 liters under standard conditions will occupy what volume under 1.2 atmospheres, at 27°C? 916

12. If the pressure on a gas at 27°C is increased 10 per cent, to what temperature must the gas be raised in order that the volume may remain constant? 570

13. What volume, expressed in liters, will a gas occupy under standard conditions if its volume at 27°C, under a pressure of 80 cm, is 500 ml? 479

14. A liter of gas is placed under double pressure, the temperature being meanwhile raised from the freezing point to the boiling point of water. What will the volume now be? 683

15. If a gas occupies a certain volume, measured at 27°C, under a pressure of 0.8 atmosphere, what must be the pressure (in atmospheres) if the volume remains unchanged at 127°C? 107

16. Suddenly doubling the pressure on a gas, originally at 27°C, releases so much heat that the volume is reduced to only 60 per cent of the original volume. What temperature (centigrade) does the gas now have? (*Hint:* If the original volume is represented by 1, the new volume, under the doubled pressure, is 0.6. Find what it would be if the temperature remained unchanged, thence infer the final temperature.) 870

17. Compare the number of molecules in a cubic centimeter of oxygen at 200°A with the number in a cubic centimeter of hydrogen at 400°A, the pressure being the same in both cases.

18. Which will diffuse the faster, methane, CH_4, or sulfur dioxide, SO_2, under the same conditions? In about what ratio?

19. A cubic foot of a certain gas weighs 0.64 oz. A cubic foot of another weighs 2.56 oz under the same conditions. Compare their molecular weights. Compare their rates of diffusion.

20. How long will it take 10 ml of hydrogen gas to diffuse through a porous wall that passes 20 ml of oxygen in 10 minutes? 125

21. What whole number almost exactly expresses the ratio of the molecular weight of carbon tetrachloride, CCl_4, to that of ammonia, NH_3? What volume of ammonia will pass through a porous wall in the same time as 20 ml of carbon tetrachloride vapor, under the same conditions? 600

22. What is the ratio of the molecular weight of carbon dioxide to that of methane? How many minutes will it take 1 liter of carbon dioxide to diffuse through a porous wall that passes 1 ml of methane in 1 second? $\sqrt{2.75} = 1.658$. 275, 276

23. What whole number comes nearest to expressing the ratio of the molecular weight of chlorine to that of ammonia? A porous wall will pass the larger *volume* of which gas in a specified time, and in roughly what ratio? It will pass the larger *weight* of which gas in that time, and in what ratio?

24. What is the average-energy velocity of a molecule of sulfur dioxide at a temperature for which it is 0.5 mile per second for a molecule o helium (a monatomic gas)? 125

25. By what percentage does the energy of an average molecule increase in passing from the freezing point to the boiling point of water? By what percentage does the average-energy velocity of a molecule increase, between these two temperatures? $\sqrt{1.366} = 1.169$. 366, 169

No student should undertake the numerical work of this or subsequent courses in chemistry or engineering without resorting to some device for saving time and reducing the risk of error in ordinary multiplication and division. A slide rule, in a few seconds, will give a product or quotient to three significant figures (sufficient for

most of the problems of this course), but it takes a few hours of practice to acquire skill. A beginner should buy a cheap rule, costing a dollar or less.

Or the four-place table of logarithms printed at the close of this book may be used. This is slower than a slide rule and takes about as long to learn to use, but gives four significant figures.

To the Instructor

This book was not meant to be plowed through from cover to cover in heavy-footed pedestrian fashion. The instructor is urged to select what he thinks fundamental or can make intellectually stimulating. Educational discipline is not to be found in the hurried survey of a wide range of topics, perhaps comprehended imperfectly, but rather in the use of a limited number of items of moderate difficulty as training in logical thinking and in the art of expressing thought.

This would seem to be an appropriate time to review the work already covered; then put into operation any plan that may have been worked out by which a superior group of students is permitted to range over more ground than the rest. If the instructor considers it important to be getting on with ordinary chemical topics he may omit or postpone much in the next few chapters that is really physics. The most vital topics are those marked ►. If these are thoroughly covered, as far as the end of Chapter 20, no difficulty will be encountered in what comes afterward.

Chapter 9

MOLES AND MOLAL PROPERTIES

► 115. Moles and Gram Atoms

In making a comparison of one substance with another it is often fairest to compare *equal numbers of molecules* rather than equal weights. This is very easily done if the molecular weights are known. Thus the molecular weights of ammonia, oxygen, and carbon dioxide are 17, 32, and 44. If we take 17 grams of ammonia, 32 grams of oxygen, and 44 grams of carbon dioxide, we have weights proportional to molecular weights, and therefore an equal number of molecules of each gas. Any comparison of one gas with another (for example, with respect to the heat that must be absorbed to produce a given rise in temperature) will then be a fair comparison.

In each of the cases just considered we have used *as many grams as there are units in the molecular weight of the given substance.* This is a *gram molecule* or *gram-molecular weight*, usually called a *mole.* (Ex. 1, 2.)

When a substance has no definite molecular weight (examples, § 40) there is, strictly speaking, no definite mole. For instance, there is no such thing as a molecule of common salt, NaCl, but only an indefinite equal number of oppositely charged ions, Na^+ and Cl^-, assembled to form a solid crystal, or perhaps dissolved to form a solution. Nevertheless the word *mole* is often used to mean what is more properly termed a *gram-formula weight* of the material, namely, *as many grams as there are units* indicated by its conventional formula, for example, $23 + 35.5 = 58.5$ grams of common salt.

A *gram atom* is as many grams as there are units in the atomic weight of an element—32 grams of sulfur, for example, or 16 grams of oxygen; and a *gram ion* is as many grams as there are units in the ionic weight—62 grams for the nitrate ion, NO_3^-, for example. (Ex. 3, 4.)

Remember that *atoms* and *molecules* are small particles; but *gram atoms* and *gram molecules* (*moles*) are definite weights of material, as in the examples just given. Go over the ideas just presented until they

are thoroughly familiar. They will recur so constantly in what follows that the student who neglects them will soon be in serious difficulty.

► 116. Molal Volume

The volume occupied by one mole of any substance, under chosen conditions (usually *standard conditions*), is called its *molal volume*, or *gram-molecular volume* (G.M.V.) One mole of oxygen, O_2, weighs 32 grams. Each liter of oxygen, under standard conditions, weighs 1.429 grams (experimental fact). A mole of oxygen, under standard conditions, therefore occupies $32 \div 1.429 = 22.4$ liters. This is the molal volume of oxygen.

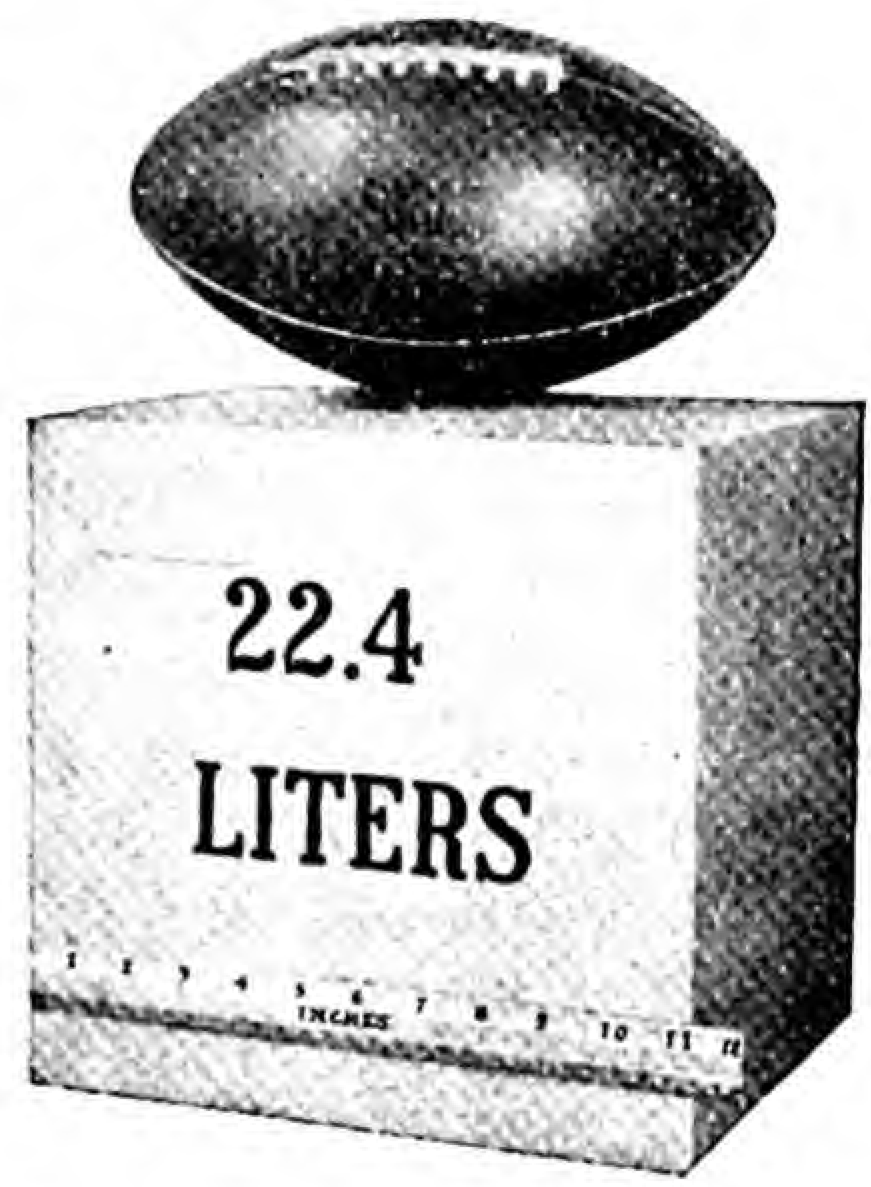


FIG. 32. The molal volume for an ideal gas under standard conditions.

If we make the same calculation with other gases, the molal volume turns out to be very nearly the same as that just obtained for oxygen, *i.e.*, roughly 22.4 liters, under standard conditions. This seems surprising, but it is readily explained. A mole is a weight of material that is large or small, in proportion as the molecular weight is large or small. It therefore represents *a definite number of molecules* (§ 182), no matter what substance is concerned. This number of molecules of a gas, under specified conditions, will occupy very nearly the same volume no matter what gas is concerned (Avogadro's Principle).

To summarize: *A mole of any gas or vapor occupies very nearly 22.4 liters, recalculated to standard conditions.*

This is one of the most important statements in this book. We have said "recalculated to standard conditions," rather than "under standard conditions," to indicate that this is what the volume would be if the gas or vapor were ideal, and could be cooled to 0°C, under atmospheric pressure, without liquefying. Actually, many vapors (water vapor, for example) would be condensed to liquid under such conditions; and because of the attraction of the molecules for one another the molal volume (under standard conditions) of readily liquefiable gases and vapors is always somewhat less than 22.4 liters. It is, for example, 22.1 liters for ammonia and 21.9 liters for sulfur dioxide. (Ex. 5–7.)

► 117. Making Use of the Molal Volume

The principle just stated can be used to calculate, approximately:

(1) The *molecular weight* of any gas of *known density.*

(2) The *density* of any gas of *known formula*, and hence of *known molecular weight.*

For example, if a gas is known to have the density of 2.5 grams per liter, then 22.4 liters will weigh $22.4 \times 2.5 = 56$ grams. This is approximately 1 mole of the gas; hence its molecular weight must be approximately 56. In practice, molecular weights determined in this way usually turn out to be a trifle high, since the molal volume is usually a little less than 22.4 liters, on account of the attraction of the molecules for one another.

As an example of the converse problem, let us find the density of carbon dioxide gas. From the formula CO_2 we calculate the molecular weight, 44. A mole is therefore 44 grams, which will occupy roughly 22.4 liters under standard conditions. The density of the gas (weight of 1 liter) will therefore be roughly 44 grams $\div$ 22.4 liters, or about 1.96 grams per liter. (Ex. 8–18.)

To determine which of two gases is the denser and in about what proportion we need only compare their molecular weights. The average molecular weight of the gases of the atmosphere is a trifle over 29. Accordingly, *we may judge whether any gas is heavier or lighter than air by comparing its molecular weight with* 29. (Ex. 19, 20.)

118. The Law of Partial Pressures

Dalton long ago observed that *the total pressure exerted by a mixture of gases is the sum of the pressures that the gases would exert if each occupied the whole space alone (Dalton's Law of Partial Pressures).* Today we know that this would be exactly true only if the gases composing the mixture were ideal.

To explain this law we need only assume that *the molecules of a gas are so far apart that molecules of one or more other gases may be slipped in among them, without perceptibly altering the frequency with which they collide with the vessel's walls, and consequently without altering the pressure that they exert.*

All the molecules in a mixture of gases at any given temperature have the same average kinetic energy of straight-line motion, $\frac{1}{2}mv^2$, whether they are heavy or light (§ 73). So if all the molecules of any gas in a mixture of gases move in any direction through the vessel and rebound, once, from its walls, the total change in kinetic energy must be proportional to the number of molecules of that particular

kind. This change in kinetic energy, each molecule rebounding *once* from the walls, is a measure of the force or *pressure* (force per unit area) that the rebounding molecules exert. In brief, *the pressure exerted on the walls of the containing vessel by any gas in a mixture of gases is proportional to the number of molecules of that gas* (and is independent of the nature of those molecules or of the presence of molecules of other kinds, at any given temperature). This is one aspect of Dalton's Law.

Commonly, we reckon proportions in *moles*. Let us suppose that we have a mixture of 10 moles of nitrogen, 2 moles of oxygen, and 8 moles of helium (20 moles altogether), and that this mixture exerts a total pressure of 1.4 atmospheres. Then the *molal pressure* (pressure per mole) is $1.4/20 = 0.07$ atmosphere. The *partial pressure* of any gas in the mixture (that is, the portion of the total pressure exerted by that gas) will be the *number of moles of the given gas, multiplied by the molal pressure:*

$10 \times 0.07 =$	0.7	atm, partial pressure of the nitrogen
$2 \times 0.07 =$	0.14	atm, partial pressure of the oxygen
$8 \times 0.07 =$	0.56	atm, partial pressure of the helium
Total	1.40	atm

We can get the same result in another way. If nitrogen contributes 10 of the 20 moles present we can say that the *mole-fraction* of nitrogen in the mixture is $\frac{10}{20} = 0.5$; similarly, the mole-fraction of the oxygen is $\frac{2}{20} = 0.10$; and that of the helium is $\frac{8}{20} = 0.40$.

The partial pressure of each gas in the mixture of gases will be its *mole-fraction, multiplied by the total pressure:*

$0.5 \times 1.4 =$	0.7	atm, partial pressure of the nitrogen
$0.10 \times 1.4 =$	0.14	atm, partial pressure of the oxygen
$0.40 \times 1.4 =$	0.56	atm, partial pressure of the helium
Total	1.40	atm

An important application of Dalton's Law is discussed in Appendix C. (Ex. 21–24.)

119. The Ideal Gas Equation

Let us represent the volume, pressure, absolute temperature, and number of moles of a confined sample of gas by V, P, T, and n. We have found that the product PV is proportional to the absolute tem-

perature (§ 104). It is also proportional to the number of molecules of gas, hence to the number of moles, n, regardless of what gas is present (Avogadro's Principle).

Now, whenever one quantity varies directly as each of two others it varies directly as their product. Hence, using the symbol $\propto$ to mean "varies as" we may write

$$PV \propto nT \qquad \text{or} \qquad PV = nRT$$

in which R is a "proportionality constant" whose numerical value (see next paragraph) depends on the units used for other variables. This is the famous *ideal gas equation*.

We have just learned that 1 mole of an ideal gas would occupy 22.4 liters under standard conditions (0°C = 273°A; and a pressure of 1 atmosphere). So, let $P = 1$, $V = 22.4$, $n = 1$, and $T = 273$. We then find $R = 0.0821$ liter-atmosphere per mole per degree absolute. Our equation, assuming this value of R, may be used for solving problems dealing with gases that are reasonably nearly ideal, provided data are given that permit n, the number of moles, to be found. Remember that V must be expressed in liters, P in atmospheres, and T as an absolute temperature, if R is taken as 0.0821. (Ex. 25–31.)

In problems in which n cannot be found, we nevertheless may know that it *remains unchanged* for any given sample of gas, as we vary the temperature and pressure. Thus with initial conditions taken as P_1, V_1, T_1, and final conditions as P_2, V_2, T_2, we have

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

as already found in § 107. (Ex. 32–36.)

120. Types of Motion for Simple and Complex Molecules

We shall presently (§ 121) describe experiments that show that the inert gases (He, Ne, A, etc.) are *monatomic*, in other words, contain only one atom in a molecule; but most other gaseous elements (H_2, O_2, N_2, Cl_2, etc.) are *diatomic*. Examples of diatomic *compounds* are HCl, CO, NO; whereas H_2O, CO_2, SO_2, are *triatomic*, and NH_3 and C_2H_2 are *tetratomic*.

The molecules of a *monatomic* gas can move in three dimensions in space: forward and back, sidewise, up and down. Combinations of these three *types of motion* or *degrees of freedom* represent all the energy of motion of a monatomic molecule. We neglect energy repre-

sented by a monatomic particle spinning on an axis, because such energy must be very small, since practically all the mass of an atom is known to be concentrated at its very center (§ 230).

But the molecules of a *diatomic* gas are capable of a more complicated motion. *Each* of the two atoms composing such a molecule may move in three independent directions in space, subject only to the restriction that the two atoms remain a fixed distance apart. Because of this restriction a diatomic molecule is not capable of $2 \times 3 = 6$ independent types of motion, but of only five, all equally probable. The five independent motions or degrees of freedom of a diatomic molecule may also be taken as a motion of the molecule as a whole in three directions in space, combined with rotation about the axes *a* and *b*, in Fig. 33. Rotation about the third axis, *c*, does not represent an appreciable amount of energy, since nearly all of the mass of the two atoms lies in this axis.

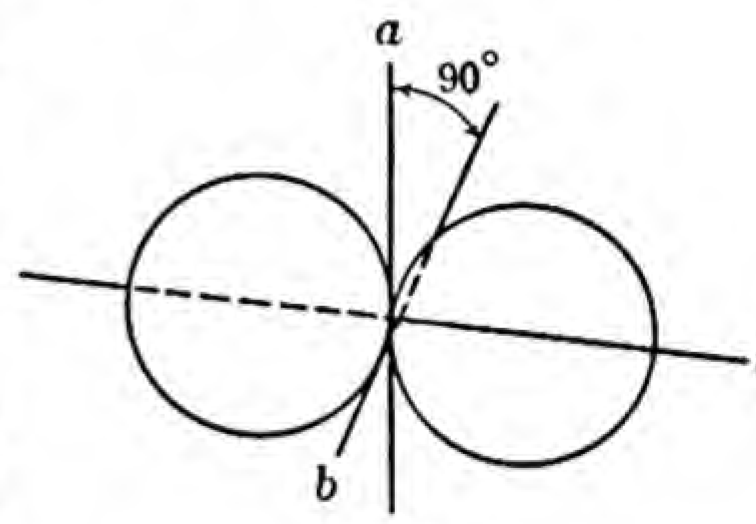


FIG. 33.

A molecule composed of three or more atoms, all in a straight line (that is, a *linear molecule*), possesses only five degrees of freedom, the same as a diatomic molecule. But if the three or more atoms are not in a straight line there are six degrees of freedom or possible types of motion, all equally probable. We may take these to be a motion of the molecule as a whole in three dimensions in space, combined with rotation about three mutually perpendicular axes.

Summary:

Monatomic molecules—3 degrees of freedom
Diatomic or linear molecules—5 degrees of freedom
Non-linear molecules—6 degrees of freedom

121. Molal Heat Capacity of Gases

When we add heat to a body we rouse all the different sorts of motion into activity of which its atoms and molecules are capable at that temperature; *the more types of motion are possible the more heat is needed to raise the temperature of the body any specified amount.* But we have just seen that monatomic, diatomic, and triatomic (non-linear) molecules are capable respectively of three, five, and six different types of motion, all equally probable. Thus the *molal heat capacity* of different gases (in other words, the quantity of heat absorbed by 1 mole in being increased in temperature 1 degree centigrade) should

stand to each other in the ratio of 3:5:6, according to the number of atoms in a molecule of each gas and their arrangement. Here are some experimental results from which the reader may readily see how nearly our anticipations are fulfilled:

MOLAL HEAT CAPACITY OF GASES, AT CONSTANT VOLUME

(at 15°C unless otherwise indicated)

Monatomic Gases		Diatomic Gases		Other Gases	
He	3.00	H_2	4.88	CO_2	6.71 *
Ne	3.00	$H_2(-180°A)$	3.30	SO_2	7.8 *
A	3.00	N_2	4.93	H_2S	8.6 *
(Anticipated value, 3)		O_2	4.97	H_2O	6.6 *
		CO	4.86	N_2O	7.94 *
		NO	4.98	NH_3	8.89 *
		Cl_2	6.58 *	CH_4	8.45 *
		(Anticipated value, 5)		(Anticipated value, 6)	

Incidentally, these results show very clearly that the inert gases are monatomic. We find a rather remarkable confirmation of our anticipation that the molal heat capacity, measured under constant volume, should be in the ratio of 3:5, according as the gas is *monatomic* or *diatomic*. But the example of hydrogen shows that molecules at very low temperatures tend to lose their energy of rotation and possess only energy of *translation* (motion in a straight line); and chlorine and all the more complicated molecules (starred, in our table) show that molecules at sufficiently high temperatures often possess extra capacity for absorbing heat beyond that anticipated—obviously because the atoms within a molecule are not really at fixed distances apart, as we have assumed, but vibrate to and fro, in a motion that grows more pronounced with increasing temperature, and ultimately causes the molecules to decompose. *A molal heat capacity (under constant volume) that is above 6 calories shows that the atoms within the molecule are being separated at greater and greater distances from one another, as the temperature is increased.* (Ex. 37–40.)

The velocity of sound in a gas is independent of the pressure, but is proportional to $\sqrt{\gamma T/M}$, in which γ represents the ratio of C_p/C_v, namely the ratio of specific heat measured under constant pressure to specific heat with constant volume, while T is the absolute tem-

perature and M is the molecular weight. Measurements of the velocity of sound in gases of known γ enable their molecular weights to be calculated. These confirm measurements of molal heat capacity in indicating that the inert gases are monatomic.

Technical Words

Gram molecule or mole, p. 124. **Gram-formula weight,** p. 124.
Gram atom, p. 124. **Gram ion,** p. 124. **Molal volume,** p. 125.
Pressure, p. 127. **Molal pressure,** p. 127. **Ideal gas equation,** p. 128.
Monatomic, diatomic, etc., p. 128. **Linear molecule,** p. 129.

Mole-fraction—the fractional part of all the moles or molecules in a mixture which are of a specified ingredient. Thus, in a solution of 1 mole of sugar in 19 moles of water, the mole fraction of the sugar is $\frac{1}{20} = 0.05$, and that of the water is $\frac{19}{20} = 0.95$.

Partial pressure—that portion of the total pressure (exerted by a mixture of gases) for which the molecules of some particular gas are assumed to be responsible. It can rarely be measured directly, but is assumed to be proportional to the relative number of moles of that ingredient; in short, it is calculated by multiplying the total pressure by the mole-fraction of the given gas.

Degrees of freedom—the equally probable terms into which the energy of an average molecule or ion may be resolved. (This definition will include potential energy, especially for crystals, § 146.)

Molal heat capacity, p. 129. **Translation** or **translatory motion,** p. 130.

Summary

§ 115. Two names given to a weight of a material that contains as many grams as there are units in the molecular weight. Similar terms, based on the weight of the atom or ion. A general term, based on the weight of a particle of any sort.

§ 116. Name given to the volume occupied by a mole of any substance. What this volume is, for an ideal gas under standard conditions.

§ 117. How one may find the density of a gas of known formula, or the molecular weight of a gas of known density.

§ 118. Dalton's Law of Partial Pressures. A simple indication of why it should be true.

Name given to the pressure exerted by any gas in a mixture of gases. Two ways in which it may be calculated.

§ 119. A statement of the ideal gas equation. Units to be used. When R may be given the value 0.0821.

When this equation is used, and what equation to use at other times.

§ 120. What is meant by degrees of freedom, as applied to the motion of a molecule. How many degrees of freedom are possessed by molecules of different types.

§ 121. What is meant by molal heat capacity.

Assuming that the types of motion represented by the degrees of freedom of a molecule are all equally probable, how the molal heat capacity of a diatomic gas should compare with that of a monatomic gas.

Why the molal heat capacity of chlorine and more complicated gases usually exceeds the anticipated value.

EXERCISES

1. Assuming that a milliliter of water weighs 1 gram, at ordinary temperatures, find the number of grams, hence the number of moles, in 1 liter of water. 555

2. A mole of cane sugar, $C_{12}H_{22}O_{11}$, is roughly what fraction of a pound? 750

3. How many gram atoms and how many moles in 320 grams of oxygen?

4. A molecule of sulfur vapor, at moderate temperatures, contains eight atoms. What is the corresponding formula? What weight of sulfur vapor is a mole? What is a gram atom of sulfur? 256, 320

5. What volume, under standard conditions, will be occupied by 160 grams of oxygen? 112

6. If 10 grams of hydrogen and 140 grams of nitrogen are mixed, how many moles will there be of each gas, and what volume will the mixture occupy under standard conditions? 500, 224

7. Write an equation for burning methane, CH_4, to form carbon dioxide and water vapor. How many moles of oxygen are needed, and how many of each product will be formed, for each mole of methane burned? What volume will each of the four gases occupy, under standard conditions?

8. Find the approximate density of chlorine, Cl_2, under standard conditions.

9. Air is a mixture containing roughly 78 molecules of nitrogen to 21 of oxygen and 1 of argon, A. Find the average molecular weight of the gases of the air, then the approximate weight of 1 liter of air, under standard conditions. 290, 129

10. A certain vapor has a density of 7.1 grams per liter, under standard conditions. Find its approximate molecular weight. 15)

11. A gas is known to be either NO_2, N_2O_4, or a mixture of both. Its density, recalculated to standard conditions, is about 3.2 grams per liter. What is your conclusion?

12. A gas, originally N_2O_4, is partially decomposed according to the equation

$$N_2O_4 \rightleftharpoons 2NO_2$$

From an original 100 moles of N_2O_4, x moles are decomposed. How many moles of NO_2 will be formed? What total number of moles of both gases is then present? What is their total weight?

13. From the result of the preceding problem find the average molecular weight, then the density of the gas mixture, both expressed in terms of x. If the density of the mixture, determined by actual weighing, is d grams per liter, show how you may find x, the percentage of N_2O_4 that was decomposed.

14. Find the approximate molecular weight of a vapor if a 100-mg sample of it occupies 20 ml, under standard conditions. 112

15. What volume will 160 mg of sulfur dioxide gas occupy under standard conditions, assuming it to be ideal? 560

16. A fuel gas is a mixture, containing 40 per cent methane, 40 per cent carbon monoxide, and 20 per cent hydrogen, by volume. How many molecules of each gas are present in 100 total molecules? How many moles in 100 total moles?

Calculate average molecular weight, hence the density of this mixture, under standard conditions. 804

17. To what centigrade temperature must oxygen be heated, under 0.8 atmosphere pressure, to have a density of 1 gram per liter? 390

(*Hint:* First find the density under standard conditions, then consider what lowering the pressure and finally what increasing the temperature will do to the density.)

18. Under what pressure, in atmospheres, does oxygen gas have the same density as carbon monoxide does under 10 atmospheres pressure, both gases being at the same temperature? 875

19. Which is the denser, methane, CH_4, or ammonia, NH_3? Carbon disulfide vapor, CS_2, or benzene vapor, C_6H_6? Oxygen or carbon monoxide?

20. Which of the gases and vapors just mentioned is lighter than air, and which heavier?

Explain why the barometer always falls as the air becomes more nearly saturated with water vapor, even if the temperature remains unchanged. (Consider the density of the mixture in comparison with that of dry air.)

21. Air contains about 1 mole of oxygen for every 4 moles of nitrogen. What is the approximate partial pressure, in millimeters, exerted by each gas at sea level? 152, 608

22. What is the mole-fraction of each gas in a mixture containing 160 grams of methane, CH_4, and 160 grams of sulfur dioxide, SO_2? If this mixture exerts a total pressure of 150 mm, what is the partial pressure of each gas? 200, 800; 300, 120

23. A sample of air, saturated with water vapor at 30°C, is confined over water under a total pressure of 740 mm. What part of this pressure is caused by the air and what part by the water vapor? (The vapor pressure of water at 30°C may be obtained from Appendix C.) 316, 708

24. When air is mingled with water vapor, in the proportion of 24 molecules to 1, what is the mole-fraction of each ingredient of the mixture, and what will be the partial pressure of each, in atmospheres, when the total pressure is 1 atmosphere? 960, 400

25. What pressure, in atmospheres, is needed to confine a mole of gas within 25 liters, at 27°C? 984

26. How many moles in a kilogram of steam or water? Calculate the volume occupied by 1 kg of steam at 100°C, under a pressure of 1 atmosphere. 555, 170

27. Liquid ammonia has a density of about 0.65 gram per milliliter at room temperature. How many moles of it are contained in a cylinder with a capacity of 1 cu ft (28.3 liters)? What volume of ammonia gas (assumed ideal) will this produce, under standard conditions? 108, 243

28. Write and balance an equation for the complete combustion of ethylene, C_2H_4. What total volume will be occupied by the carbon dioxide and water vapor produced, if the ethylene burned occupies 1000 cu ft, under the same conditions? 400

29. One cubic meter of carbon dioxide gas, at 27°C, under 760 mm pressure is how many moles? How much does it weigh? 406, 179

30. At what centigrade temperature will a mole of any ideal gas, under 1 atmosphere pressure, occupy 25 liters? 315

31. How many moles of ideal gas in a sample occupying 2.5 liters, under 0.9 atmosphere pressure, at 27°C? 913

32. A gas occupies a certain volume at 27°C, under 1 atmosphere pressure. What pressure must be applied to confine it within the same volume at 127°C? 133

33. Under what pressure, in millimeters, will a gas at the boiling point of water occupy the same volume as it does under 1 atmosphere pressure, at the freezing point of water? 104

34. Doubling the pressure on a gas is found to decrease its volume to 60 per cent of its original volume. Has the absolute temperature meanwhile increased or decreased, and by what per cent? 200

35. Two measurements are made. One reports a gas volume at 30°C, under a pressure of 1.1 atmospheres. The other reports an equal volume under standard conditions. Do the reports both relate to the same sample of gas? Explain how you know.

36. Water at 100°C has a density of 0.958 grams per milliliter. What volume is occupied by a kilogram of water at this temperature? Compare this result with that in Exercise 26 to determine the ratio of the volume of steam produced to the volume of the water vaporized, at the boiling point of water. 104, 163

37. Liquid water has a heat capacity of very nearly 1 calorie per gram per degree centigrade. Calculate the heat needed to raise the temperature of 1 mole of liquid water from 15° to 16°C; also the corresponding value for a mole of water vapor, heated while confined under constant volume. 180, 660

38. What should be the molal heat capacity of hydrogen chloride gas, HCl? Then what should be its specific heat? 500, 137

39. Does the energy stored in a sample of gas under a piston change with the pressure on the piston, if the temperature remains constant?

40. If more air is pumped into a tank of compressed air, is the total stored energy proportional to the mass of stored air? Is it proportional to the pressure which the stored air exerts?

Chapter 10

LIQUIDS

► 122. The Molecular Condition of Liquids

If we possessed microscopes about a thousand times as powerful as any until recently made, we believe that a liquid would be revealed as a jostling throng of molecules, in the most frenzied agitation. We would then readily perceive that the molecules of a liquid are crowded very closely together; yet even when they seem to touch they vibrate back and forth, since they are not rigid spheres, like marbles, but deformable, like rubber balloons.

In ordinary experience, such motion would gradually die away and the particles come to rest. But ordinary experience will not always guide us in the realm beyond the microscope. The particles we are observing with our imaginary supermicroscope continue in the most energetic motion, however long we continue to observe them. We realize that they have been in motion from the dawn of creation, and that they will continue to move as long as matter itself continues to exist, since matter and energy are equally eternal.

Now let us watch for details. We see that every particle in the interior of the liquid is opposed by a *resistive force*, whenever it collides with and presses against its neighbors; thus it is presently brought to rest and made to recoil. Then in swinging away from its neighbors the particle tends to be slowed down by the *attractive force* that the particles have for one another—a consequence of their strong attraction for one another. So each particle moves incessantly, gaining or losing energy in repeated collisions with its neighbors, and gradually wandering away from its original position, like a man elbowing his way through a crowd on New Year's Eve.

We can now understand why gases under very high pressures are nearly indistinguishable from liquids. The interior of a liquid differs from that of a gas chiefly in having its molecules crowded more closely

together. By putting a gas under sufficient pressure, we can compel its molecules to approach one another so closely as to approximate the internal structure of a liquid. Nevertheless, there is a difference: If we diminish the pressure, the molecules of a compressed gas scatter indefinitely; those of a liquid attract one another with sufficient force to prevent indefinite scattering. Hence the liquid comes to possess *a definite upper surface.*

► 123. Associated Liquids

The very great quantity of heat needed to vaporize water and ammonia in comparison with most other liquids clearly indicates that much more than the usual amount of energy needs to be expended in removing molecules from liquid water or liquid ammonia and dispersing them as vapor. But why? A clue is found in the observation that *water and ammonia enter into chemical union with a great many other substances.* Liquids such as gasoline and carbon tetrachloride, by contrast, not only require less energy in being vaporized but are also chemically rather inert. It seems reasonable to believe that the molecules of water combine not only with other kinds of molecules, but also with *one another*, to form complex molecules of indefinite size. Similarly for ammonia. The extra quantity of heat that disappears in evaporating these liquids would then be explained by assuming that extra energy needs to be expended in tearing down the complex molecules, to form simple ones.

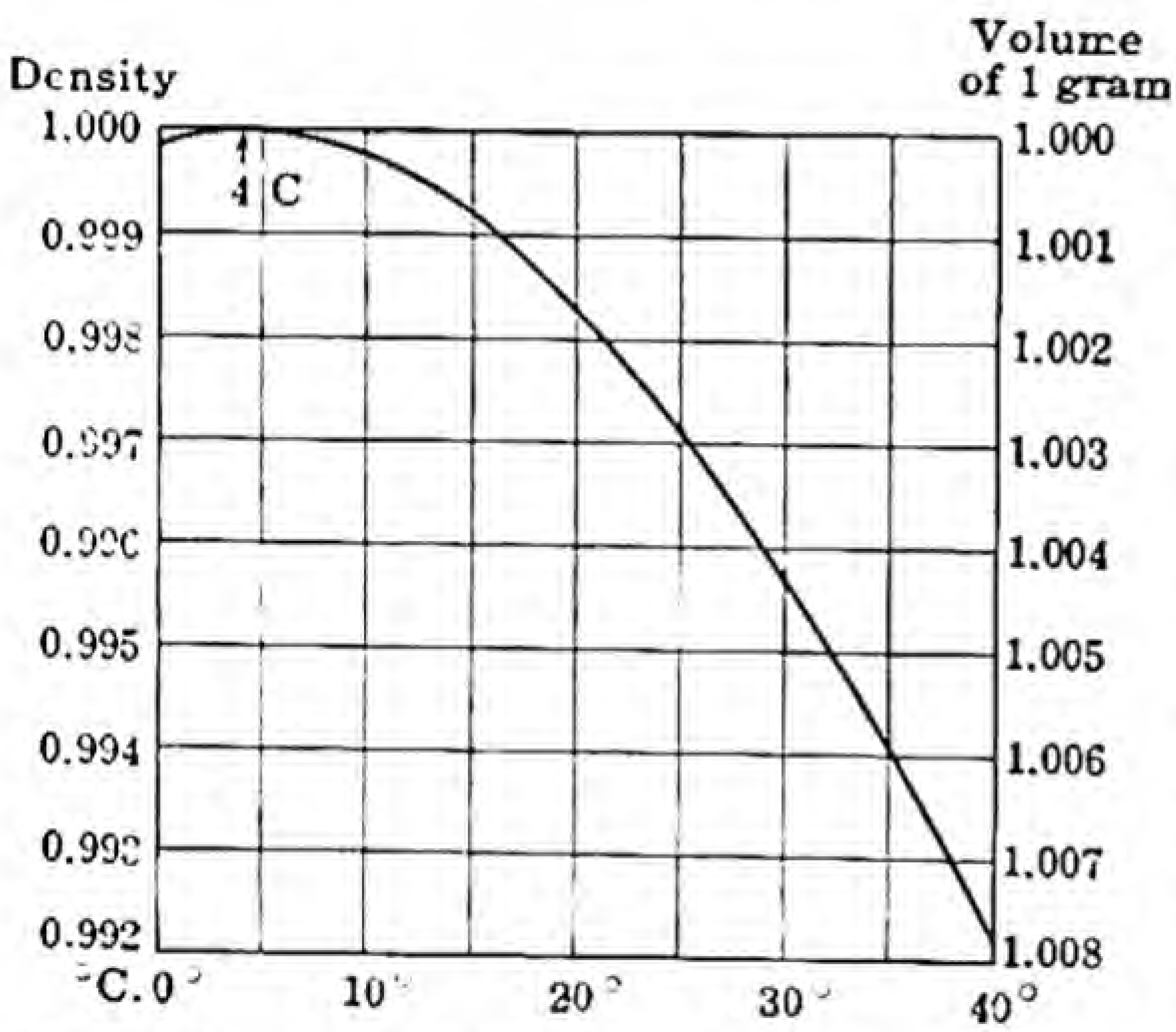


FIG. 34. Water has its maximum density at 4°C.

Liquids (such as water or liquid ammonia) whose molecules are formed by the reversible union of two or more simple molecules are said to be *associated.* Not all the molecules of such a liquid are associated at any one time, nor are they permanently associated. A condition of equilibrium is reached, in which the association of simple molecules, to form more complex ones, proceeds at the same rate as the dissociation of complex molecules, already formed. If a molecule

of liquid water is formed by the association of n molecules of water vapor, we might write:

$$n\mathrm{H_2O} \underset{\text{Dissociation}}{\overset{\text{Association}}{\rightleftharpoons}} (\mathrm{H_2O})n$$

The associated molecules of water are probably not properly represented by any definite formula, but are large aggregates of indefinite complexity. *As the temperature is raised, the proportion of associated molecules in an associated liquid decreases steadily.* The dissociated molecules can be packed a little more closely together than the large associated molecules. Consequently, as the temperature of water is increased from 0° to 4°C increasing dissociation causes a slight increase in density; but as the temperature is raised still higher the increase in density due to dissociation is more than offset by a decrease due to expansion. Otherwise expressed, water has its maximum density at 4°C (Fig. 34). (Ex. 1.)

Liquids (such as benzene or chloroform) which are not very reactive chemically are *unassociated.* Their molecules, in the liquid state, are identical with those of the same materials in the vapor state.

▶ 124. Viscosity

Viscosity is a measure of resistance to flow, most easily observed in liquids that are conspicuously "thick" or viscous. The viscosities of two liquids may be compared by comparing the lengths of time needed for a chosen volume to be forced through a given tube of small diameter. *The higher the viscosity of a liquid, the more time is needed for any chosen volume to be forced through a tube of chosen length and internal diameter.* In making this comparison we must, of course, apply the same pressure to both liquids, or we must make allowance for the fact that rate of flow is proportional to the pressure applied. For fluids of very high viscosity, such as tar or asphalt, viscosity may be compared by dropping a steel ball into a sample of given depth, observing the time necessary for the ball to sink to the bottom.

"Molasses in January" reveals that viscosity increases with lowered temperature. By imperceptible degrees, as the temperature is lowered, highly viscous fluids gradually stiffen into *plastic solids*, such as beeswax, and these into glassy or *vitreous solids*. Plastic solids fail to flow until a certain minimum pressure is applied, whereas true fluids will flow, though slowly, with the smallest measurable pressures. A glacier appears to have plastic flow, though it really yields by fracture to form crevasses and pressure ridges, or by melting, momentarily, at

points where the pressure is greatest (for pressure lowers the melting point, whenever melting results in a decrease in volume).

125. How We Account for Viscosity

We can readily account for the viscosity of fluids. When we set a fluid to flowing bodily through a tube we add some extra motion, lengthwise along the tube, to the confused and irregular motions that the molecules of fluid previously had. But before any molecule near the walls of the tube has proceeded very far it collides with molecules of the wall and loses a part of its motion in the direction in which the fluid as a whole is flowing. Rebounding from the wall with diminished forward velocity, it collides with other molecules and diminishes their forward velocity. Thus the fluid is observed to move very slowly in layers near the wall, more rapidly at a greater distance from the wall, and most rapidly along the central axis of the tube.

If the explanation just given is true, then even gases should possess measurable viscosity, though their molecules are relatively far apart. Indeed we easily see that the viscosity of a gas or liquid must be related not only to the average *distance between its molecules* but also to their average *speed* and to their *size*, since all three of these factors determine the frequency with which the molecules collide with one another. Conversely, if we know the average distance of the molecules of a gas from one another, a measurement of its viscosity will enable us to calculate the size of its molecules (as already suggested in § 114).

If we ask what has become of the *energy* that the molecules lose when their forward motion through the tube is retarded by collisions with their neighbors, the answer is evident. This energy is transferred to neighboring molecules, which in consequence move with increased energy *in random directions*. This random motion is heat. In brief, *the energy of forward motion through the tube is converted into heat in proportion as the forward motion is retarded.*

If we perform work on a fluid, in forcing it through a tube, the work is in part converted into *heat*, as just described, in consequence of the collisions of the molecules with one another. What remains is available for giving the liquid *kinetic energy* of forward motion through the tube or *potential energy* with respect to the earth (in elevating the fluid to a higher level). This application of the principle of Conservation of Energy forms the basis of the science of *hydraulics*.

Finally, let us observe that *thermal conductivity* (*i.e.*, conductivity for heat) depends on the transfer of energy by collisions between mole-

cules, in other words, on the same factors that determine viscosity. No wonder, then, that viscosity and thermal conductivity tend to rise and fall together, as we compare one fluid with another.

126. Forces Acting on a Surface Molecule

The simplest things in nature are often the most mysterious. Primitive man, before the dawn of history, observed that water spread through fabrics that happened merely to be wet at one end, and that oil rose in wicks. The lamps of ancient times were basins filled with oil in which small wicks were floated; oil ascending through a wick replaced that consumed by the flame at the top. The ascent of sap in trees is in part due to the same cause.

But why should water spread through a fabric, and why should oil rise in a wick? It is no explanation to label the phenomenon "capillary action." To understand what really happens, we must begin with a study of the forces acting on a surface molecule. Consider a molecule (*a*, Fig. 35) *in the surface of a liquid*. It is attracted by neighboring molecules, within and beneath the surface, in the directions shown by the arrows. Since these forces must fluctuate as *a* moves about, their *resultant*[1] must also fluctuate; nevertheless the average value of the resultant over any appreciable interval of time must be directed downward.

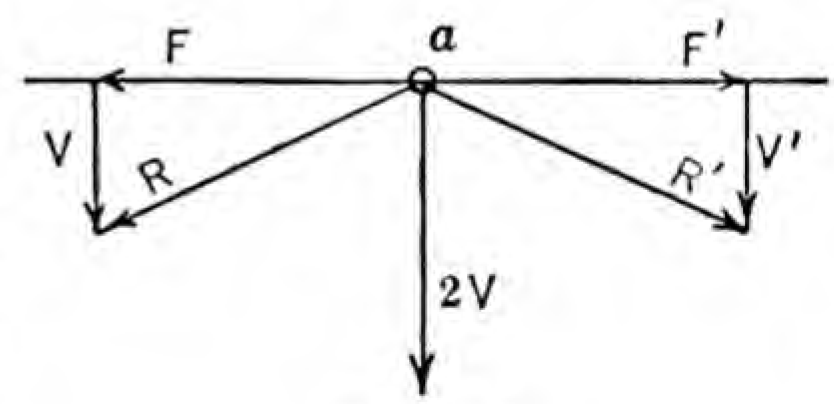


Fig. 35.

Let us divide these attractive forces into two groups, on each side of a vertical plane passed through *a*, perpendicular to the printed page. The resultant of forces at the left of the plane will be in the general direction R, and of those at the right will be in the general direction R'. These two forces, averaged over any appreciable interval of time, will be equal. Each may be resolved into a horizontal force, F or F' and a vertical force, V. The total vertical force, acting downward on the molecule, will then be $2V$. Though the given molecule is acted upon by the two opposite and equal horizontal forces, F and F', and by the vertical force $2V$, it tends to remain near its original position, since the downward force, in the long run, is offset by forces set up by collisions with underlying molecules.

The explanation just given is a fair indication of the origin of forces acting on a surface molecule, but in one respect is a gross exaggera-

[1] The single large force which would have the same effect as all the individual small forces, acting together.

tion. These forces do not really act through distances very much greater than the diameter of a single molecule. In brief, *practically all the force exerted on any molecule is due to its nearest neighbors—those that are practically in contact with it.*

127. Surface Tension

In Fig. 36 we have a perspective drawing in which the molecule in the preceding figure (with the forces acting on it) is shown again, together with other surface molecules, in a straight row *ab*, 1 cm long. Let us assume that there are 20,000,000 molecules in this row. Each of them is urged to the right by the force *F;* hence there is a total force of 20,000,000 *F*, acting *in the surface*, perpendicular to the line *ab*, and tending to move this row of molecules toward the right. An equal force acts in the surface on the opposite side of *ab*, tending to pull the row of molecules off toward the left.

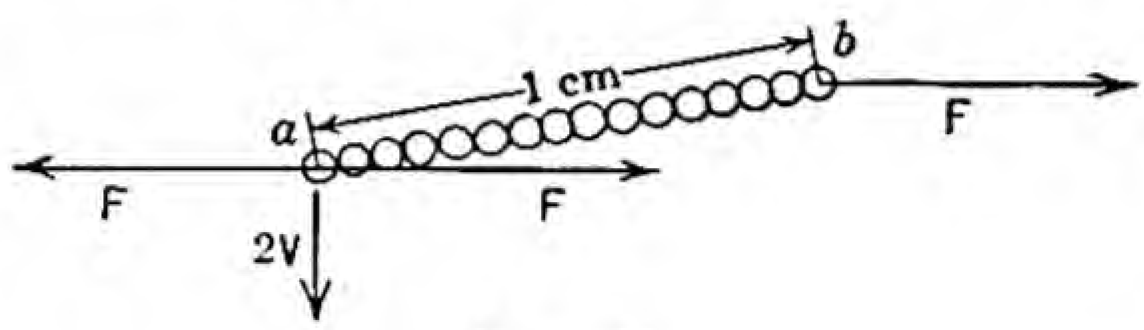


FIG. 36.

The total force just considered, on either side of the line *ab*, is called the *surface tension* of the liquid. It is *a force in the surface*, calculated for any straight line in the surface 1 cm long, and tending to move the molecules lying on this line sidewise toward their neighbors.

Surface tension is created by the mutual attraction of surface molecules and other molecules, *within* and *beneath* the surface. It is of course somewhat altered if other molecules are present in the space *above* the surface. For example, the surface tension of a liquid exposed to air or its own vapor is very different from the surface tension at the interface between this and another liquid—for example, at the interface between water and an overlying layer of oil.

Surface tension (expressed in dynes) is measured by the work (in ergs) that must be expended in creating 1 sq cm of new surface, by bringing up new molecules from the depths of the liquid, and ***orienting*** them, in a closely packed array, in the surface of the liquid. This is what happens in blowing a soap bubble, for example.[2]

128. Some Effects of Surface Tension

The pull of surface tension tends to diminish every liquid surface to the smallest possible area. The smallest area, for an object of any

[2] Observe that a soap bubble has both an inner and an outer surface, hence the increase in surface area, in expanding the bubble, is twice the increase in the outer surface of the bubble.

given volume, happens to be that of a sphere. For that reason, droplets of liquid tend to assume a spherical form. The smaller a droplet and the lower its density the less it is flattened by the pull of gravity, and the more nearly it approaches a truly spherical shape.

Surface tension tends not only to diminish every liquid surface, but also to pack the surface molecules together in *the smallest possible area* and to orient them in *parallel positions*. In the same manner, the closest packing of books is attained when they are all turned on edge, in parallel positions, on a library shelf.

Since the surface molecules are drawn very strongly toward one another by the pull of surface tension, the surface resists being stretched or penetrated, much as it would if covered by a film of rubber. The analogy is not a very good one, however, for the tendency of a rubber film to contract increases in proportion as it is stretched, whereas the tendency of the surface of any pure liquid to contract is fixed and definite for that liquid at any given temperature, and does not alter as the surface is increased. This is evidently because new molecules are brought up from beneath the surface as they are needed to keep the average distance from molecule to molecule constant at the given temperature, in spite of the increase in surface. With a liquid containing a trace of impurities the surface tension may not remain constant as the surface is extended.

On account of the tension in the surface film, water beetles and other insects are able to glide about on the surface of still water, without ever breaking through. Needles or even a small boat made of wire gauze may easily be floated on water, because supported by the surface film; but a small drop of alcohol in the neighborhood of such a vessel will so diminish surface tension that the surface film gives way, and the vessel instantly goes to the bottom, as dramatically as if sunk by a torpedo.

A *wetting agent* is a substance that favors the adhesion of a liquid to the surface of another liquid or the surface of a solid. An effective wetting agent is always composed of elongated molecules, whose two ends possess very distinct and almost opposite properties. One end of such a molecule must dissolve in the liquid to be employed, while the other end must remain undissolved. The undissolved end must be capable of adhering to the solid or of dissolving in the liquid that is to be wet. The wetting agent serves as an intermediate phase, concentrated in the very surface of the liquid. Its molecules link the surface of the liquid to the surface of the solid as effectively as the edges of two pieces of fabric are linked by the claws of a zipper.

Soap is the most familiar and most widely used of the many substances possessing such surface-gripping molecules. At one end of every molecule of ordinary (sodium) soap is the —COONa group of atoms, which readily dissolves in the surface of the water, leaving the remainder of the soap molecule (a long "hydrocarbon chain," $CH_3 \cdot CH_2 \cdot CH_2 \cdot \cdot \cdot CH_2 \cdot CH_2 \cdot CH_2$—) undissolved and protruding outward. This hydrocarbon chain will, however, dissolve in oil. Soap

Courtesy of the Hazard Advertising Corporation

FIG. 37. Floating is no problem to a duck because its feathers, protected by a natural film of oil, hold millions of tiny, buoyant air bubbles. But the duck on the left had to deal with a solution of Aerosol, which so diminished the surface tension of water that it penetrated the duck's feathers and displaced the air. So the duck, wet to the skin, came near drowning.

therefore permits water to wet oil, and so brings about the dispersion of kerosene and other oils in water, in preparing emulsions that serve, for example, as orchard sprays.

During recent years dozens of effective wetting agents have been synthesized. They are far superior to soap in that they are not decomposed by acids or precipitated by hardness in water. A good example is the substance with trade name Aerosol. A molecule of this substance contains a sulfonate group, —SO_3Na, which is drawn into and dissolves in water, leaving two long hydrocarbon chains, which remain undissolved. Water can thus be made to wet oily and greasy materials, in brief, to wet any surface to which the two hydrocarbon groups will adhere, or in which they will dissolve.

Wetting agents have many important applications in industry. A few tenths of 1 per cent of an effective wetting agent will insure the uniform wetting, hence the uniform dyeing, of fabrics dipped into a dye bath; also the better adhesion of glues to materials to be glued together; and the better wetting of materials of all sorts by protective coatings applied by brushing, spraying, or dipping.

Wetting agents have some other useful properties, though these are not always proportionate to their effectiveness as wetting agents:

They aid the dispersion (subdividing) of particles of lampblack or pigment in the preparation of inks or paints, the dispersion of graphite in certain types of lubricants, and the dispersion of clay in the preparation of ceramic products. Some of them have important detergent (cleansing) properties.

All wetting agents decrease the surface tension of liquids to which they are added, hence some of them are effective in the production of foam.[3] Since many of them are unaffected by acids they lend themselves to spectacular lecture experiments in which hydrogen or other gases are generated in presence of acids and collected in a stable foam.

129. The Rise or Fall of Liquids in Capillary Tubes

Where a liquid touches the walls of a containing vessel there is a contest between two opposing forces:

1. The mutual attraction between the molecules of the wall and the molecules of liquid. This force tends to draw neighboring liquid molecules toward the wall.

2. The force of surface tension, which tends to contract the surface into the smallest possible area, hence to pull the surface molecules of liquid away from the wall.

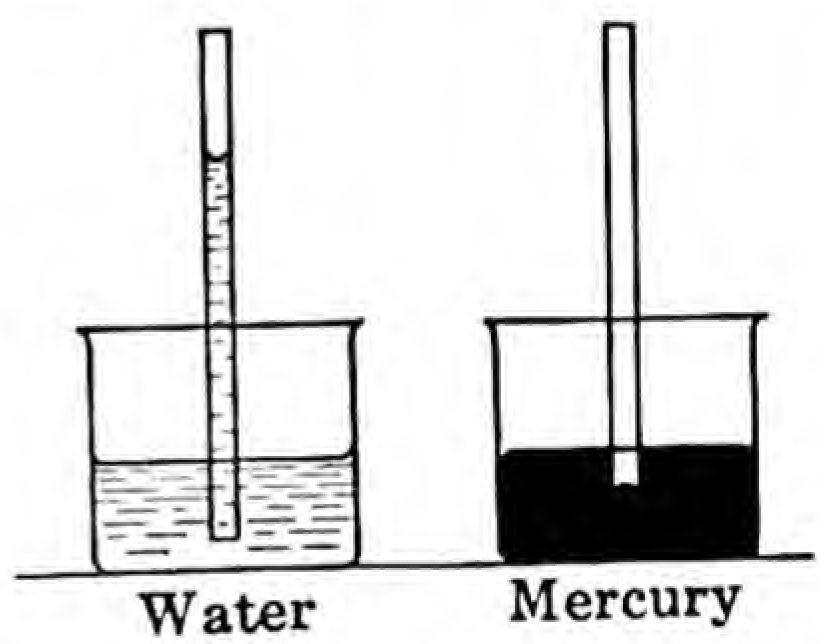


FIG. 38. Elevation or depression of a liquid in a capillary tube.

If the first of these two forces is the stronger the liquid *wets* the wall. More than that, molecules of liquid move toward and creep up the wall until this tendency is balanced by the force of gravity, acting on the elevated particles. That explains the rise of liquids in capillary tubes (including the pores of wicks) which the liquids happen to wet (Fig. 38).

The rise of a liquid in a capillary tube is directly proportional to the surface tension of the liquid at that temperature; it is inversely proportional to the density of the liquid and to the diameter of the tube (*Law of Capillary Rise*). (Ex. 2, 3.)

On the contrary, the force of surface tension may be greater than the attraction of the molecules of the wall for the surface molecules of liquid. The liquid then fails to wet the wall and is depressed, rather

[3] Foam producers sometimes decrease and sometimes increase the surface tension of the liquid to be made to foam; in addition, some material must be present that will serve to stabilize the foam.

than elevated, in a capillary tube. Mercury in glass capillaries is a familiar example. In any case, the surface assumes the shape that makes the potential energy of the surface a minimum (§ 67).

130. The Surface Tension of Different Liquids

The surface tension of water at room temperature is about 70 dynes, as compared with about 20 or 30 dynes for unassociated liquids, such as benzene or carbon tetrachloride. We have evidence in this that the molecules in the surface of water are oriented very strongly and packed together much more closely than they are in the body of liquid. Fused salts have a surface tension of 200 dynes or more—evidence of strong electrical forces between their particles.

The surface tension of liquid metals is still higher: 400 to 500 dynes for low-melting metals, just above their melting points, and about 1100 dynes for molten copper. This shows that the attractive forces between the atoms of a metal are of a very special kind and very powerful. The high surface tension of metals is of practical importance in *soldering*, since it results in strong capillary action, which causes the liquid solder to penetrate between two metal surfaces that have been cleaned, then pressed together. (Ex. 4.)

As the temperature of a liquid is raised its surface tension decreases, because the surface molecules are farther apart the higher the temperature, and because they gradually lose the orientation that favors strong attractive forces within the surface plane. Moreover, molecules of vapor, accumulating above the liquid, exert an attraction for the surface molecules that tends to offset the downward pull of the underlying molecules of liquid. At a sufficiently high temperature liquid and vapor become identical, and the surface separating them disappears (§ 154). Every molecule in what was previously the surface is now subject to an equal pull in all directions; hence the surface tension is zero. (Ex. 5, 6.)

131. The Spreading of Oil on Water

We have seen that the pull of surface tension not only makes the surface of a liquid occupy the smallest possible area, but also causes the molecules in the surface to be oriented in parallel positions. Further evidence for surfaces being constructed in this way is found in the spreading of oil films on water.

Mineral oil, being insoluble in water, merely rests upon the surface of the water in shallow pools or lenses (Fig. 39) of indefinite extent,

and probably a few molecules thick. When a ship is hove to in a stormy sea, with canvas bags of mineral oil attached to the sea anchor, thin pools of oil drifting past the ship smooth the water in a remarkable way, by preventing the waves from breaking into spray. When giant waves in a hurricane stumble over shoals, the crests are torn away in swirling fountains, which rear over the ship mast-high, and crash down on the decks like avalanches. A few buckets of mineral oil, dribbled on the surface of the sea in pools a few molecules thick, then tame a million tons of water.[4] This nearly magical result is perhaps due to the high surface viscosity of the oil.

FIG. 39.

Oily acids, in contrast to mineral oil, spread out over water to form films that cover a much greater area than is ever covered by a like amount of mineral oil. It was long ago guessed that such thin films of oily acids (such as oleic acid or palmitic acid) are actually one molecule deep. The proof came with experiments in which the area covered by the invisible film of oily acid was measured in a very simple way, as shown in Fig. 40.

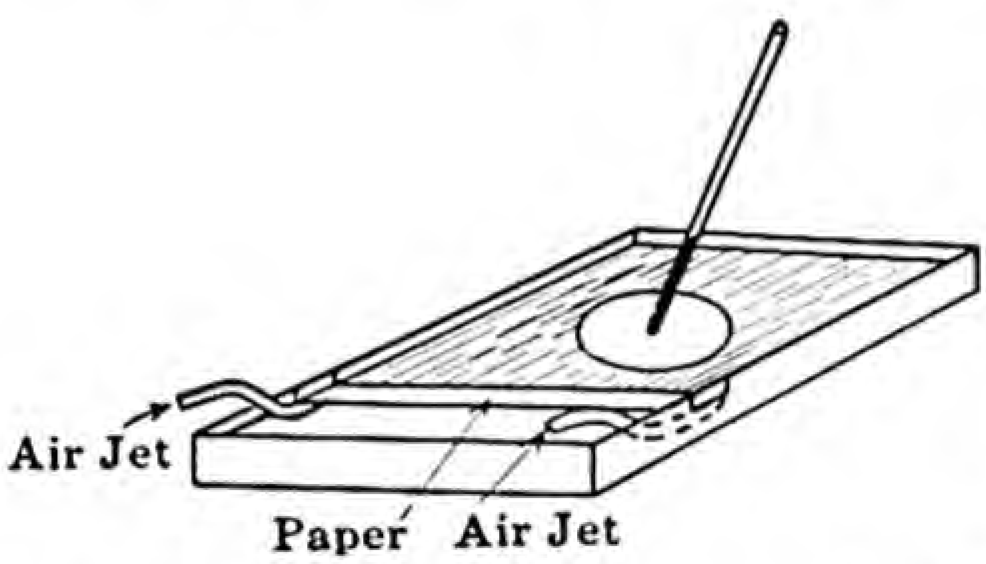


FIG. 40. Air jets, at the margins of a paper barrier, prevent the escape of the talcum-dusted surface, until the area of the clear pool of oily acid can be measured.

The water was first cleared of accidental films of grease by sweeping it with paper strips. Its surface was next dusted with talcum powder. Then a trace of the oily acid, dissolved in ether or benzene, was added through a capillary tube. The ether or benzene dissolved or evaporated, leaving an oily film that pushed back the talcum powder in all directions, to form a clear pool whose area could be measured.

Evidence has been obtained that in some of these *unimolecular films* one end of the molecule of the oily acid is dissolved in the water, leaving the other end to protrude into the air! In other words, the molecules of oleic acid are spindle-shaped affairs, which are strongly oriented in the surface, as shown in Fig. 41. From measurements of the area of surface film it has been possible to deduce the length and cross section of a single molecule. (Ex. 7, 8.)

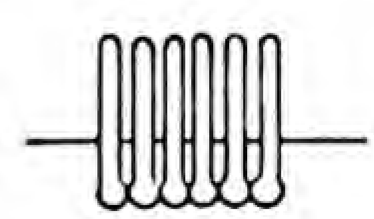
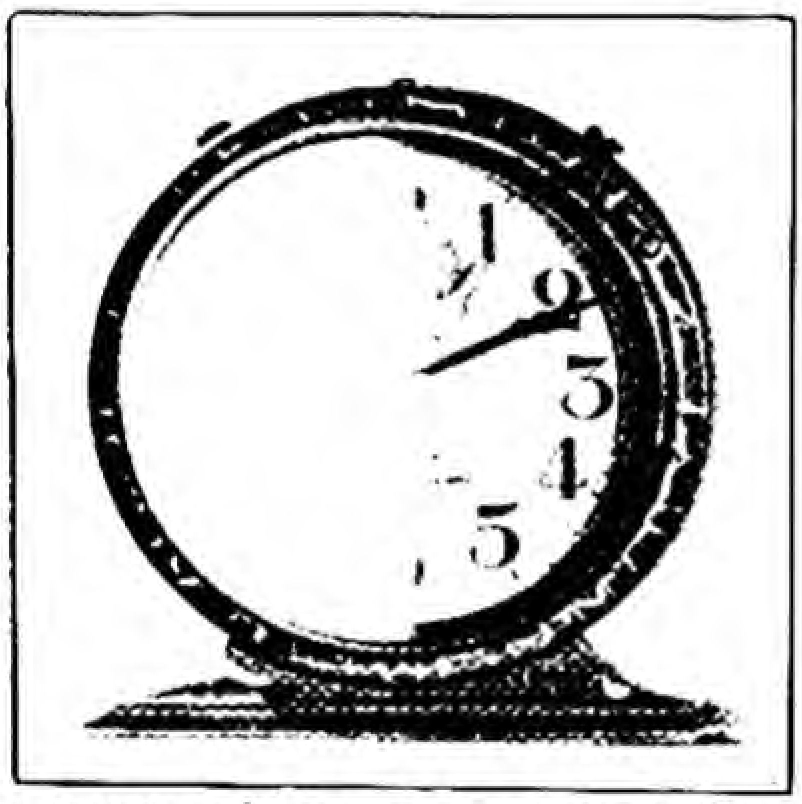


FIG. 41.

[4] A vivid description is found in *In Hazard* (Richard Hughes, 1938).

132. More About Surface Films

In other experiments a thin film of oily acid was confined between a fixed and a movable barrier, both made of paraffined copper strips. The force that needed to be applied to the movable barrier, to confine the oily film within any given area, could readily be measured by adding weights to a balance pan or in other ways. These experiments showed that films of different substances, one molecule thick, behave in different ways. Some are as readily compressible as *vapors*, but others are apparently *liquids* or *solids*. A liquid film can often be recognized by the fact that particles of talcum powder, dusted



Courtesy of the General Electric Co.

FIG. 42. One half of this clock face has been given a coating that eliminates glare due to reflected light, and so renders the glass nearly completely transparent.

upon it, keep moving rapidly, whereas in other instances the powder lies quietly upon the film, as if the molecules composing the film were linked to form a rigid solid, one molecule thick! We may crumple such a solid, but we cannot otherwise compress it.

An interesting application of these facts has recently been discovered (1938). A unimolecular film, spread upon water, can be picked up by slipping under it a sheet of glass. Then additional films, each one molecule thick, can be laid down upon the first, until the glass has received an oily or waxy coating any desired number of molecules thick. On attaining a certain thickness this coating acts to prevent the reflection of light that otherwise takes place at the surface of glass; in brief, the glass becomes invisible and completely transparent. Anyone who wears glasses will appreciate the promise of practical usefulness in such a discovery. The problem is to make the very thin surface coating adherent enough and strong enough to resist being rubbed off.

During the recent war the lenses of military cameras were given a coating which greatly decreased the reflection of light from the lens surface, and prevented the condensation of surface moisture. The

effective speed of the lens was thus considerably increased, and photographs taken on dark or misty days showed much better definition.

133. Questions Still To Be Answered

Having thus explained some of the characteristics of liquids, with the aid of our ideas about molecules, we may return to the world of ordinary events—we came near saying to the world of reality. But are events that we perceive with our unaided senses any more real than those we trace only by means of precision instruments, guided by the light of reason?

As usual, our explanations seem to have raised more questions than they have cleared away. That is not surprising. The more one learns about anything the more one will find to arouse further interest and challenge the alert intelligence. We have shown that the liquid state is made possible by the attraction that molecules may exert upon one another when they approach very closely. But why should this attraction be very strong in water (which is consequently easily liquefied), but very weak in hydrogen, oxygen, or nitrogen (which are consequently hard to liquefy)?

We have accounted for surface tension; but the very high surface tension possessed by molten metals leads us to wonder what special sort of forces must exist between metallic atoms to lead to this result.

We have seen that certain oily liquids, placed on water, sometimes remain as coherent droplets and sometimes spread upon the surface of the water as solid, liquid, or perhaps even vapor films, one molecule deep. We account for these different results by differences in solubility between different parts of the film-forming molecules. But this leaves us to wonder what makes a particular group of atoms or a particular kind of molecule more soluble than another.

We have seen that the molecules of certain liquids cling together in groups or clusters of molecules, thus giving a higher molecular weight to the substance in the liquid condition than it possesses as vapor; but we have not explained why certain liquids have a much greater tendency than others to behave in this manner. Answers for some of these questions will be attempted in later chapters; for others, as the reader has doubtless guessed, the answers are still unknown.

Technical Words

Associated, unassociated, pp. 136, 137. **Viscosity,** p. 137.
Vitreous solids, p. 137. **Thermal conductivity,** p. 138.
Resultant force, p. 139.

Surface tension—a force, acting in the surface of a liquid, due to attraction between neighboring molecules within and just beneath the surface, and tending to diminish the surface.

Unimolecular film—a film one molecule thick.

Summary

► § 122. In what respect liquids resemble highly compressed gases. A practical test to distinguish a liquid from a compressed gas.

► § 123. A name given to a reaction in which,simple molecules, all of the same kind, combine to form complex molecules. Two liquids for which this tendency is especially great. Name given the reverse process.

How one may judge, from the energy expended in vaporizing a liquid, whether it is associated or unassociated. What other evidence may sometimes be used.

Temperature at which water has maximum density, and presumed explanation.

► § 124. A word expressing resistance to flow, as one layer of a liquid slips over another.

A name given to solids that may be deformed or molded; another, given to glassy solids.

§ 125. How we account for viscosity. What becomes of the energy represented by the work done in forcing a liquid through a tube.

§§ 126, 127. Sketches to show what forces act on molecules in the surface of a liquid, and how these result in surface tension.

§ 128. How surface tension accounts for spherical droplets, water beetles, effect of soap on fabrics. What practical uses are made of wetting agents.

§ 129. Two opposing forces where a liquid comes in contact with a wall.

What determines whether a liquid will wet a wall. What then happens. The contrary case.

§ 130. How the surface tension of water compares with that of unassociated liquids. Whether the surface tension of liquid metals is high or low. Application in soldering.

§ 131. How mineral oil is sometimes used to quiet water about a ship in a storm.

What special kind of spreading is sometimes observed with oily liquids. How one may measure the area that has been covered with a film of oily acid.

§ 132. What we mean by unimolecular films. Three different types of such films. An application.

Exercises

1. A liter of water at 4°C (Fig. 34) will have what increase in volume if heated to 20°C?
170

2. The surface tension of water at room temperature is about 72 dynes. That of alcohol is roughly 24 dynes. The density of alcohol is about 0.8 times that of water. To what height will alcohol ascend in a capillary tube in which water ascends 24 mm?
100

3. What must be done to the diameter of the capillary tube just mentioned to double the height of ascent of both liquids?

4. The density of molten copper is about 8 times that of water. Its surface tension, just above the melting point, is about 16 times that of water at room tem-

perature. Compare the height to which molten copper will ascend in a capillary tube with the height to which water will ascend in the same tube at room temperature.

5. A fine foam has a much greater surface than one composed of coarse bubbles. As an aid to forming such a foam would you attempt to raise or lower the surface tension of the foaming liquid? (Consider the energy that needs to be expended.)

6. Should a wick in which an unassociated liquid is to be elevated by capillary action have capillaries of a smaller or larger diameter than one designed to elevate water? Why?

7. Oleic acid has a molecular weight of roughly 300. One-tenth milligram of that acid is roughly how many moles, expressed as $\frac{1}{3}$, multiplied by a negative power of 10 (Appendix E)?

8. If a mole of any substance is roughly 6×10^{23} molecules (§ 182), how many molecules in the preceding sample of oleic acid? $2\times$

If the sample covers an area of 400 cm^2, what area represents the cross section of a single molecule? (Use powers of 10.)

Chapter 11

SOLIDS

► 134. General Characteristics of Solids

A *solid* is distinguished from a fluid (gas or liquid) by ability to maintain its shape in spite of moderate forces (for example, gravity and surface tension) that tend to deform it. The ability of a solid to resist being altered in shape is termed *rigidity*. One aspect of rigidity is *hardness*, the ability to withstand being dented or scratched. Solids may be arranged in a rough *scale of increasing hardness*, by placing them in such an order that *each will scratch those preceding it in the list:* (1) talc, (2) rock salt (or gypsum), (3) calcite, (4) fluorite, (5) apatite, (6) feldspar, (7) quartz, (8) topaz, (9) corundum, (10) diamond. The number here assigned to each substance gives its position in the arbitrary scale of hardness. A substance judged to be intermediate in hardness between feldspar and quartz would then be said to have a hardness of about 6.5.

The hardness of metals is commonly determined (1) by measuring the diameter of the indentation made by a hardened steel sphere, pressed against the metal with a definite pressure (Brinell hardness test); or (2) by measuring the height of rebound of a small hammer dropped against the surface the hardness of which is to be estimated.

When the rigidity of a solid is overcome by the application of sufficient force it may assume and retain a new shape. Solids which will do this are said to be *plastic*. Other solids, instead of being plastic, are conspicuously *brittle*. A sufficient force will break or shatter them.

Steel, silk, and the tungsten filaments of electric light bulbs are examples of solids having conspicuous *tensile strength* (ability to resist being broken by a direct pull). Brick, concrete, and many building stones have no very great tensile strength, but have considerable *crushing strength* (ability to withstand being broken by application of pressure).

► 135. Crystalline vs. Non-Crystalline Solids

The word crystal was first applied to ice and to quartz (which was found everywhere in nature in gleaming, massive crystals, that must have appeared to primitive man to be some heat-defying form of ice). Only in the seventeenth century was the term *crystal* or *crystalline* applied to a whole group of solids, usually recognized by their being bounded by plane surfaces and by their possessing definite melting points. Crystalline solids are sometimes termed *true solids*.

Non-crystalline or *amorphous* (*Greek:* formless) solids are usually only apparently non-crystalline. Glass, wax, charcoal, paraffin, rubber, and textile fibers are examples. Some of these are merely so soft that their regular crystalline form is obscured. Impurities may prevent others from assuming clear-cut crystalline forms. In still others, the liquid from which the solid material has been separated is so viscous that the formation of crystals of visible size is prevented.

If a solid lacks definite crystalline form and appears to be completely structureless (glass, for example) we ordinarily conclude that conditions were unfavorable for the formation of crystals large enough to make their presence known except by tests based on the use of X-rays (which frequently reveal the presence of crystals of less than microscopic size, § 140).

If a solid softens over a considerable range of temperature (glass, asphalt, or wax, for example) we conclude that it is probably *a mixture of materials*, which might all be found to possess definite melting points, if separated from one another. Solids having the apparently random internal structure and irregular fracture of glass are sometimes termed *vitreous solids*.

Textile fibers, plastic sulfur, and rubber are revealed by X-rays to assume the characteristics of crystalline solids whenever they are *stretched*. This astonishing fact will be explained in later chapters. So we end by concluding that practically no solid material is completely structureless or non-crystalline. An evident exception is the light-dimming metallic film that slowly gathers on the inner surface of cheap electric-light bulbs, from atoms of metallic vapor, which evaporate from the filament and are deposited on the glass in random positions, wherever they happen to strike.

► 136. Determining the Melting Point of a Solid

Every crystalline solid, if pure, melts at a definite temperature, provided that heat does not first decompose it. Ice, for example, melts at 0°C, and ordinary (rhombic) sulfur at 112.8°C, these tem-

peratures being altered only by a few hundredths of a degree, even by increasing the pressure manyfold.

A very pure crystalline solid will often "melt sharply," that is, will begin to melt and will be completely melted within a temperature range not exceeding a few hundredths of a degree. An impure crystalline solid, on the contrary, may begin to melt and finish melting over a range of several degrees, according to the amount of impurity that happens to be present in it.

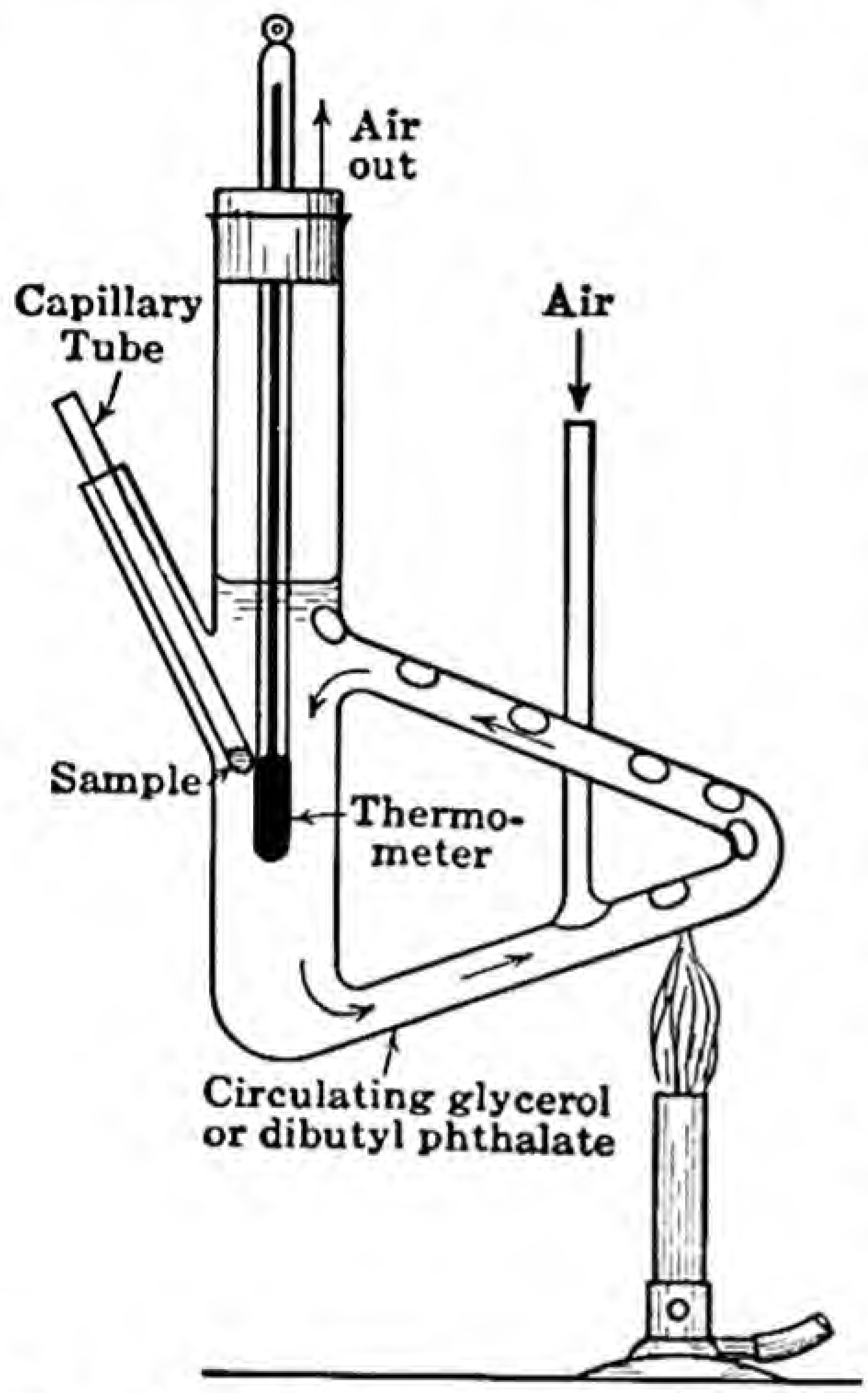


FIG. 43. Determining the melting point of a solid.

Submit a sample of a crystalline solid to a chemist for identification and he will frequently begin by determining its melting point (Fig. 43). If this agrees with the melting point of a material of similar general characteristics, as recorded in some published "table of melting points," he presumes that his unknown sample is of this material. Incidentally, from the sharpness of its melting point, he will gain an idea of how pure it is. Then comes the crucial test: *He mixes the sample being tested with a little of the material which he judges it to be.* If it still melts at the same temperature as before, his presumption is almost certainly right. If its melting point is now lower than before he knows he has been mistaken—for *usually a mixture of two different substances of nearly equal melting points will melt at a lower temperature than either one alone.*

► 137. Crystalline Solids Possess Directional Properties

All crystals except those of the cubic system (§ 141) possess *directional properties*—that is, properties which vary with the direction through the crystal in which they are measured. Important examples are conductivity for heat and electricity, and *index of refraction* (p. 168), which in turn depends on the velocity of light through the material. A few crystals are *doubly refracting.* By this we mean that any ray of light entering them is resolved into two separate rays, which proceed at different speeds through the material and are consequently refracted or bent aside through different angles. If

one looks through such a crystal (for example, a crystal of calcite, Fig. 44) objects beyond it will appear double. An interesting and important fact about these two beams of light is that they are both plane polarized.[1]

An important directional property possessed by many crystals is *cleavage*—capacity for being split along planes determined by the internal structure of the material. A diamond cutter does not really cut diamonds, to bring them into shapes that favor a brilliant appearance; he applies pressure in carefully chosen directions to split or

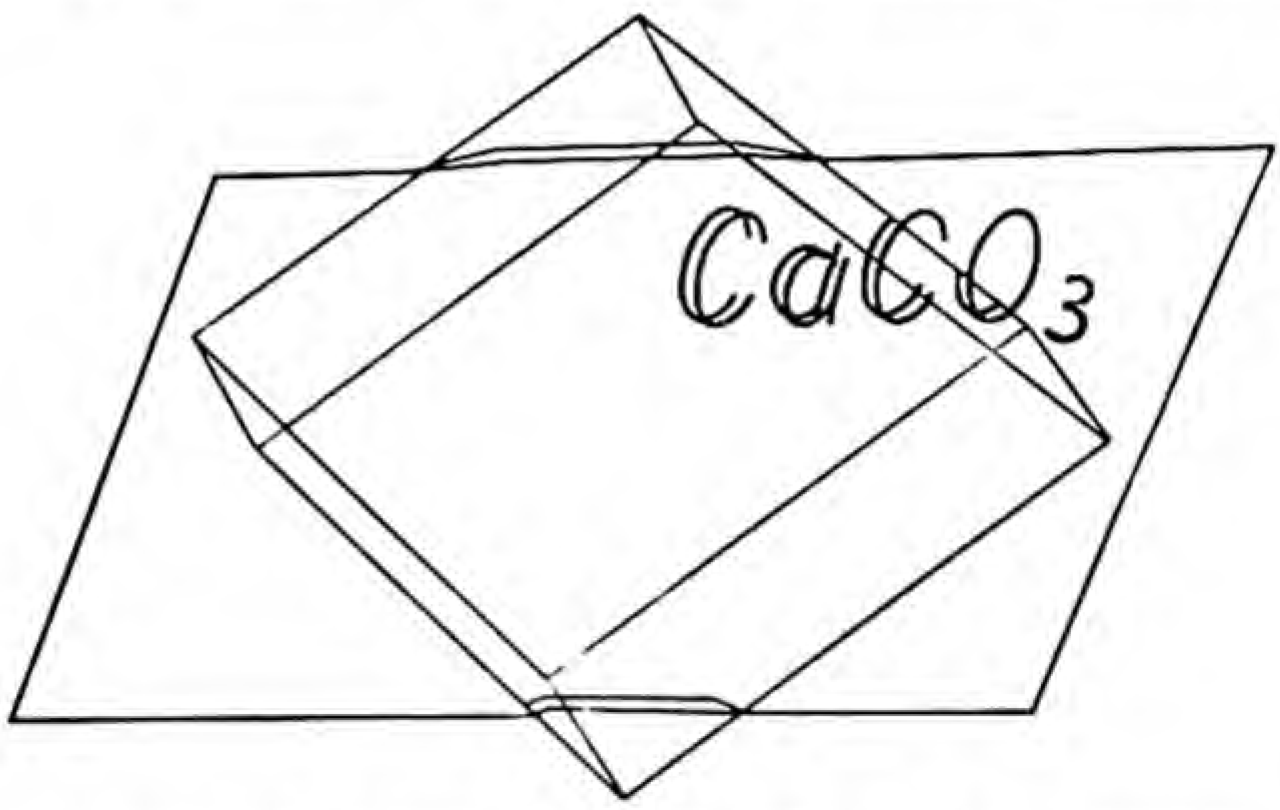


FIG. 44. Cleavage crystal of calcite, showing double refraction (birefringence).

cleave the stone along definite natural *cleavage planes*. Common salt crystals, no matter how irregular, readily cleave into cubes. Mica cleaves into thin plates, and asbestos into fibers.

138. Crystals Possess Definite Interfacial Angles

Whether a crystalline solid actually does or does not attain a symmetrical form will depend on whether or not it is produced by deposition from a liquid or a vapor that reaches the growing crystal freely on all sides. Figure 45 (next page) shows a perfect crystal, together with an imperfect one, in which the face *a* is enlarged at the expense of its neighbors (because solid material, in the growth of the crystal, was *prevented* in some manner from freely reaching this face, while neighboring faces were being covered by successive layers of material, thus extending the given face sidewise, in all directions, and so increasing its area). *The most prominent faces on a crystal are those on which new material has been deposited most slowly from the liquid or vapor phase.*

It is easy to see that the face *a* makes the same angles with neighboring faces in the perfect crystal as it does in an imperfect one. In

[1] By this we mean that the wave of electrical force, accompanying the beam of light, is restricted to a single plane.

other words, *there is a definite and invariable angle between any two faces of a given kind of crystal, whether the crystal has actually attained a symmetrical form or not* (*Law of Definite Interfacial Angles;* De Lisle, 1783). (Ex. 1.)

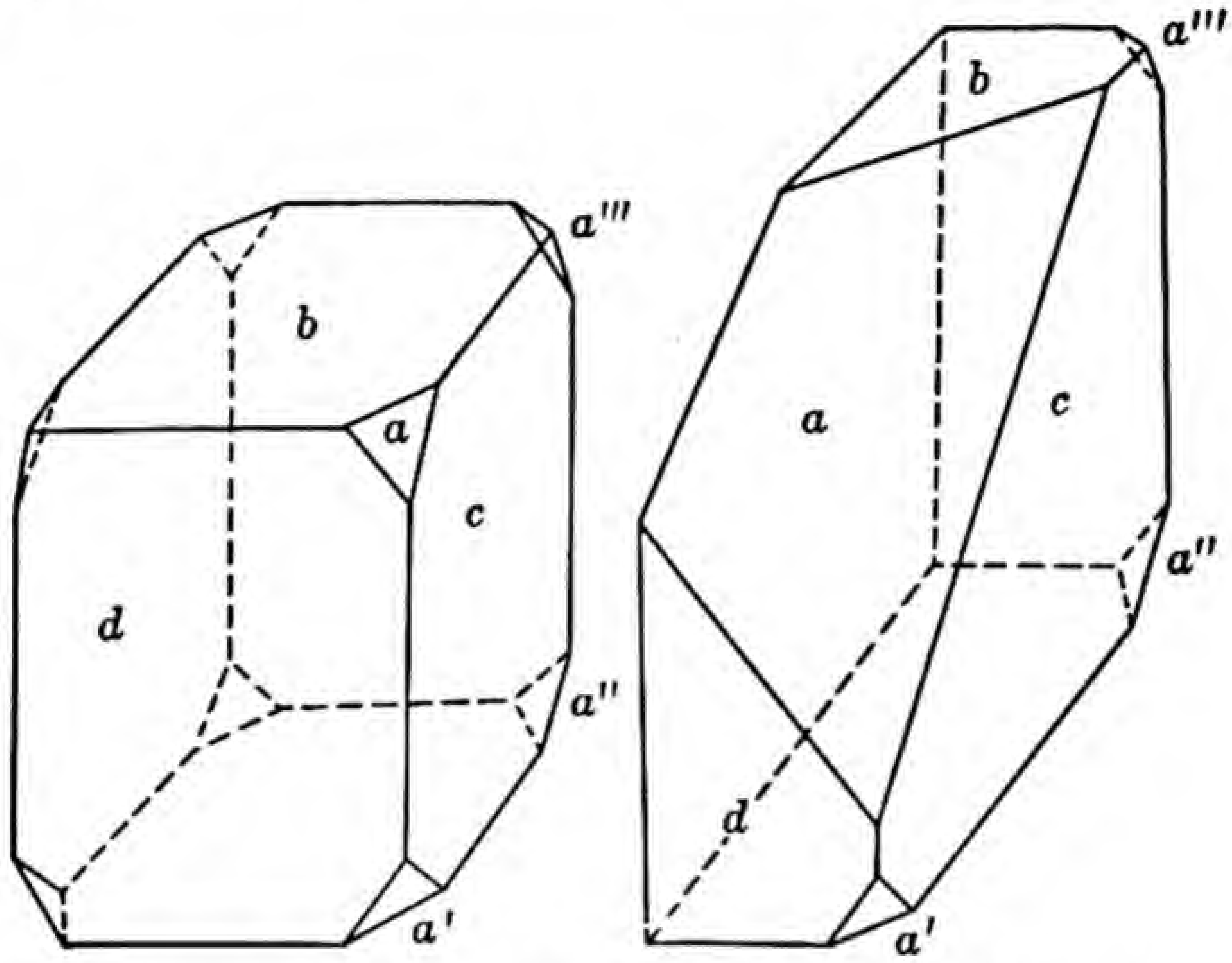


FIG. 45. The Law of Definite Interfacial Angles.

► 139. Some Conclusions from a Pile of Blocks

The plane surfaces of crystals, their tendency to assume symmetrical external forms, and their directional properties long ago suggested that the particles composing them must be arranged in some regular way in space. By analogy, a compact pile of bricks or blocks owes its plane surfaces and regular external form to the orderly arrangement of the bricks or blocks composing it.

The presence of different kinds of faces, of unequal development, all on the same crystal, is then very easily explained. In the pile of blocks shown in Fig. 46 we see a horizontal face, *a;* vertical faces, *b;* an inclined face, *c;* and a pyramidal face, *d.* Although *c* and *d* appear not to be perfectly smooth, we can see that they would be indistinguishable from smooth, plane surfaces if the blocks composing the pile were as small as atoms and molecules are supposed to be.

The angles that these four faces of our pile of blocks make with one another are evidently determined by the *dimensions of the individual blocks.* Still other faces, with other slopes, would have been present (Fig. 47) if the steps in our pile of blocks had been two or three blocks high, but only one block wide; or two or three blocks wide, but only one block high; or perhaps three blocks high and two blocks wide. Thus we account for the multiplicity of faces of most actual crystals, and also for the fact that the *slopes of different faces*

of the same crystal are related as small whole numbers. This is one form of the *Law of Rational Indices* (Haüy, 1784; and Weiss, 1809). (Ex. 2.)

By stripping away a few blocks in Fig. 46, we may easily produce a new and larger plane, parallel to any given face, such as *d*. This shows us once more that, if deposition of new material on any face of a crystal is retarded in any manner during the growth of the crystal, that particular face will become more prominent.

By adding an impurity to the solution from which a crystal is separating, we may sometimes hinder the growth of certain faces more than that of others, and thus change the external form of the crystal

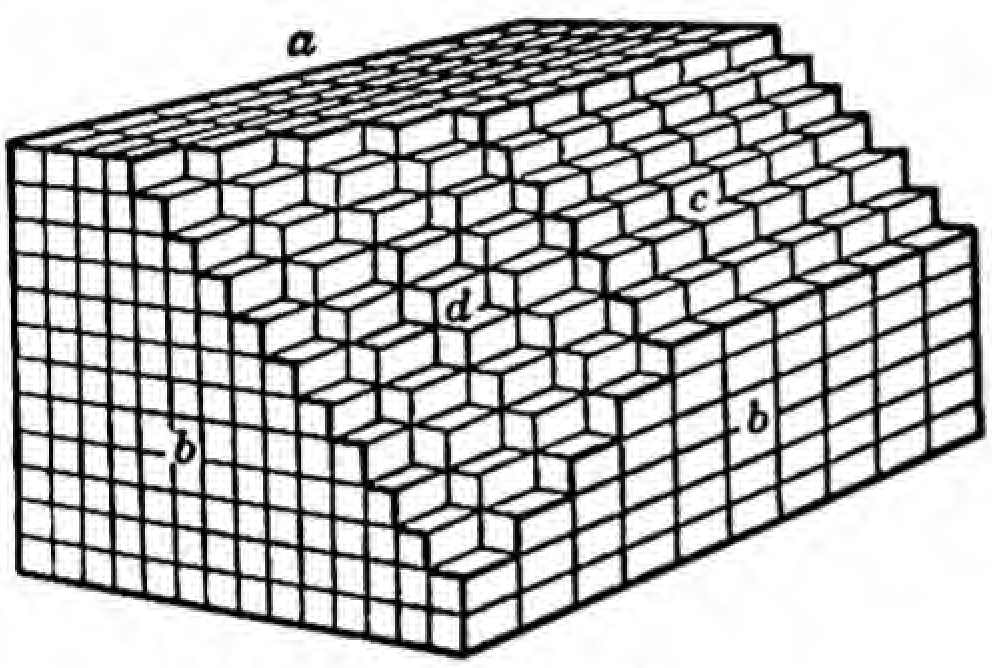


FIG. 46.

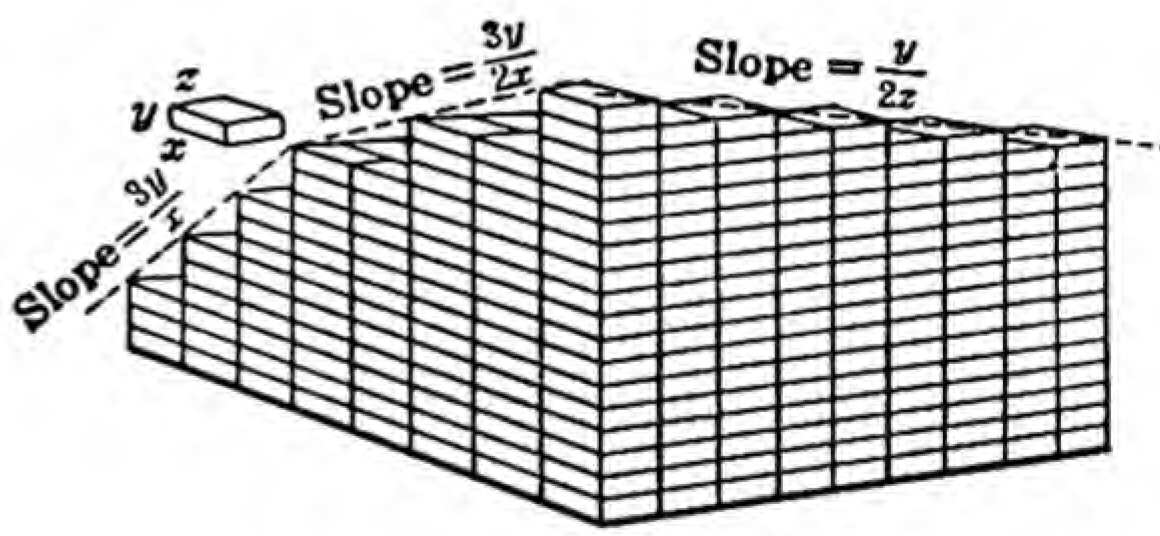


FIG. 47.

completely. Nevertheless our pile of blocks, or the two crystals compared in Fig. 45, will convince anyone that, no matter whether a face is well developed or very small, its angles with neighboring faces will depend on the dimensions of an individual block, and will be definite and constant.

► 140. Crystal Structure Revealed by X-rays

The suspicion that crystals are constructed after the manner of a pile of blocks or bricks, by assembling atoms and molecules in regular arrangements in space, remained only a surmise during more than two centuries. Then X-rays (1914) brought evidence of its truth. When a narrow beam of X-rays is (1) passed through a large crystal or (2) reflected from it, or even (3) when the beam is scattered in a somewhat irregular manner by passage through a crystalline powder, it will produce patterns of light and shadow on a photographic plate (Figs. 48, 49). From such patterns anyone with sufficient mathematical insight may deduce (at least for the simpler types of crystals) not only how the atoms are arranged in space with respect to one another, but also what the actual distance is from the center of one atom to the center of any of its neighbors.

We give here only the final result: *The arrangement and distance apart of atoms within crystals have been determined for many of the most important types of crystals, with a percentage accuracy that surpasses that with which distances are ordinarily determined in laying out a city or in erecting a building.* In the best instances such *interatomic distances* are now known within about 1 part in 30,000, corresponding in accuracy to an error of only 1 inch in a measured distance of nearly

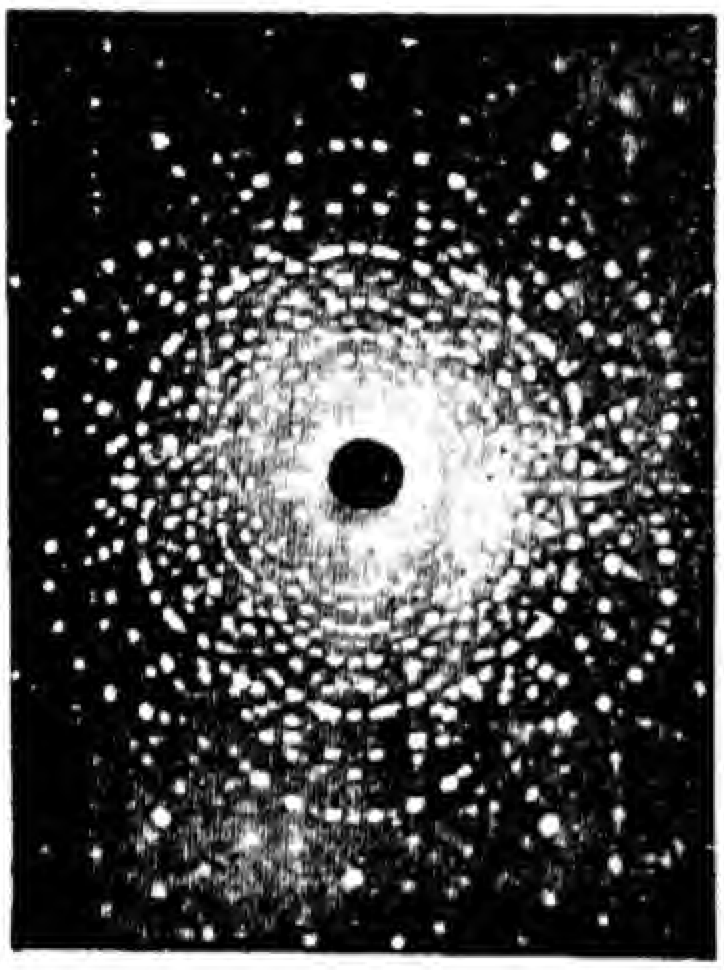


FIG. 48. A narrow beam of X-rays traverses a large crystal, revealing a 6-fold axis of symmetry, parallel to the beam.

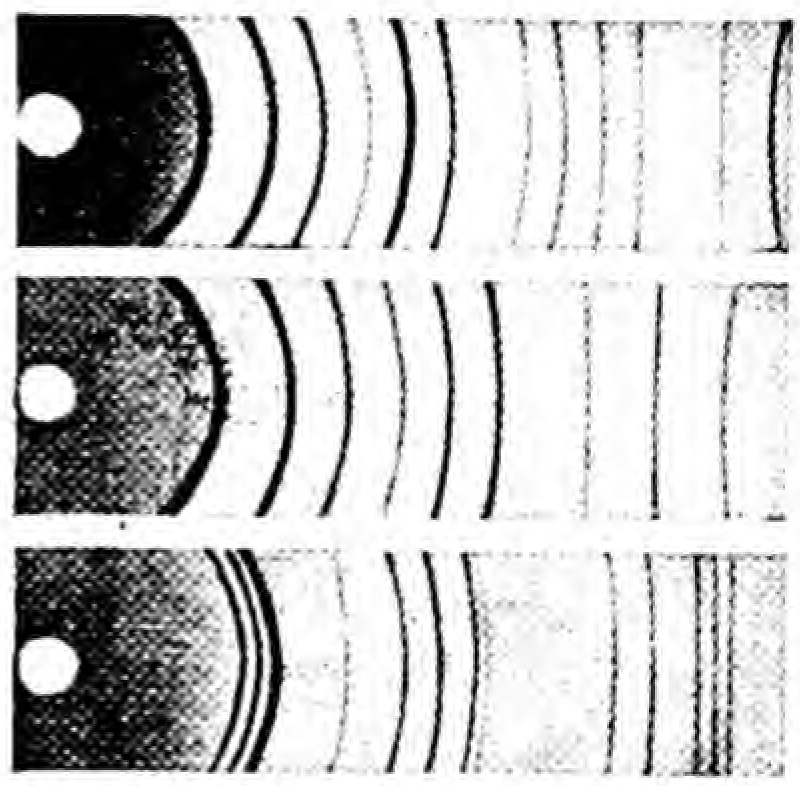


FIG. 49. Patterns formed by passage of X-rays through crystalline powders.

half a mile! In a crystal of common salt, NaCl, the center-to-center distance between atoms (ions), along an edge of the crystal, is 2.814 Ångström units, *viz.*, 2.814×10^{-8} cm.

141. Types of Symmetry

We have said that most actual crystals are imperfect, owing to being grown under conditions in which solid material is somewhat impeded in reaching and being deposited on certain faces. These faces are consequently exaggerated, and the crystal as a whole is lop-sided or distorted. Crystals also sometimes develop as joined twins and show still other abnormalities.

From an imperfect crystal it is nevertheless often possible to see what the perfect or ideal form of that material would be. Sometimes the ideal form may be obtained by splitting an imperfect crystal along cleavage planes.

An ideal crystal has one or more *axes of symmetry*. If the crystal is rotated about such an axis one will discover 2, 3, 4, or 6 different

positions, in the course of a single revolution, in which a former arrangement of faces and angles is repeated, so that the crystal presents exactly the same appearance as before.

For example, consider the cube (Fig. 50). An axis passed through the centers of any two opposite faces is a 4-fold axis of a symmetry. The cube has three such axes, all mutually perpendicular and of the

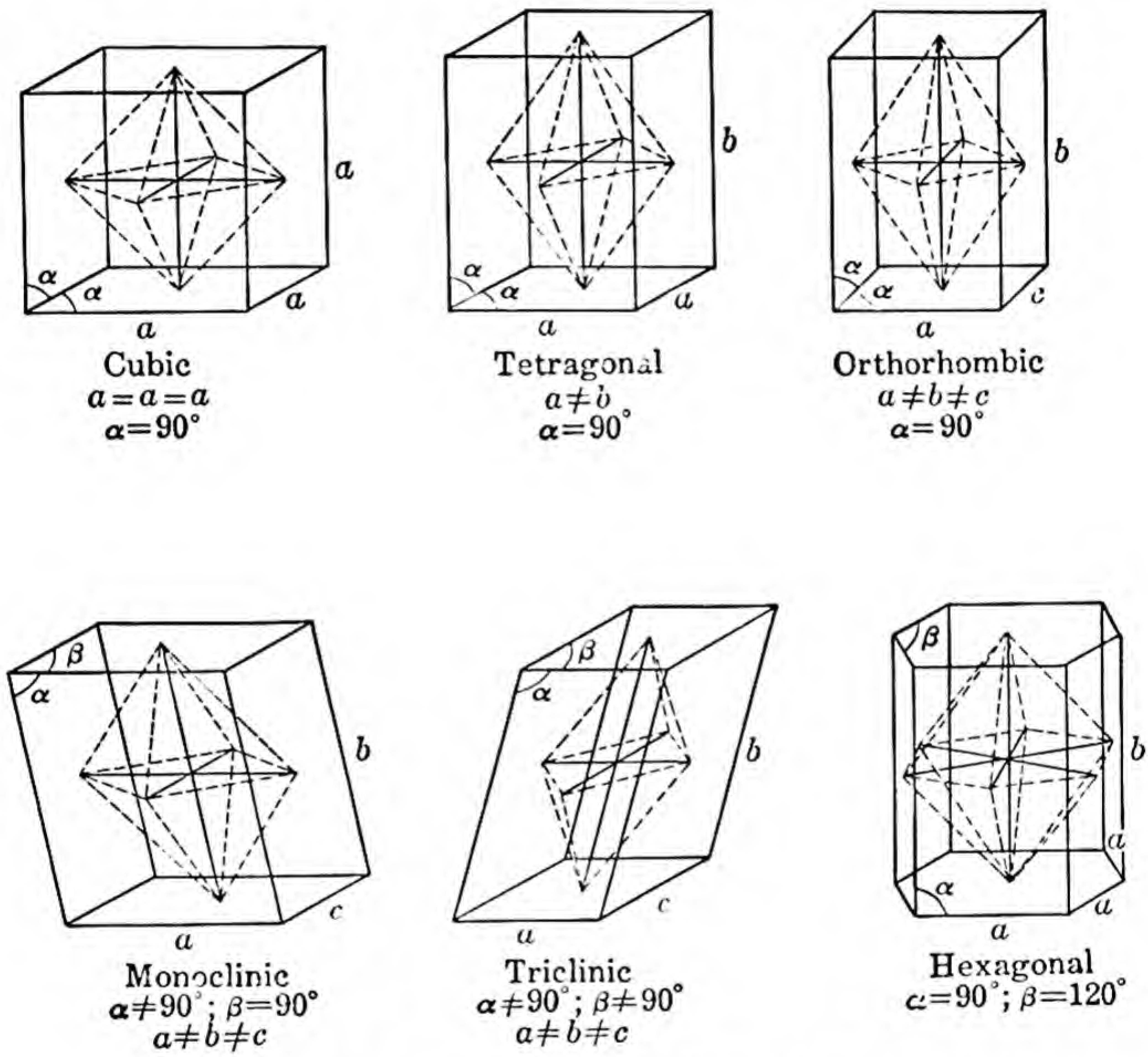


FIG. 50. Six fundamental types of crystal symmetry.

same length, as shown in the figure. The cube also has four 3-fold axes of symmetry (each passing through diagonally opposite corners) and six 2-fold axes of symmetry (each passing through the mid-points of opposite edges). Can you find them, in the figure? (Ex. 3.)

Ideal crystals may be classified into six different classes, according to the number and character of their highest-ordered axes. Details are shown in Fig. 50.

But the external symmetry of these six classes of crystals is of course due to the symmetrical arrangement in space of the atoms or

molecules that compose the crystal. Every atom or molecule in the crystal is surrounded by a certain number of nearest neighbors, packed closely against it and touching it on all sides, as in Fig. 51. The crystal as a whole may be considered as having been constructed by infinite repetition of a small group of particles, filling an imaginary *unit cell.*

The particles in every unit cell are arranged according to one of fourteen fundamental types of symmetry, which determine the six

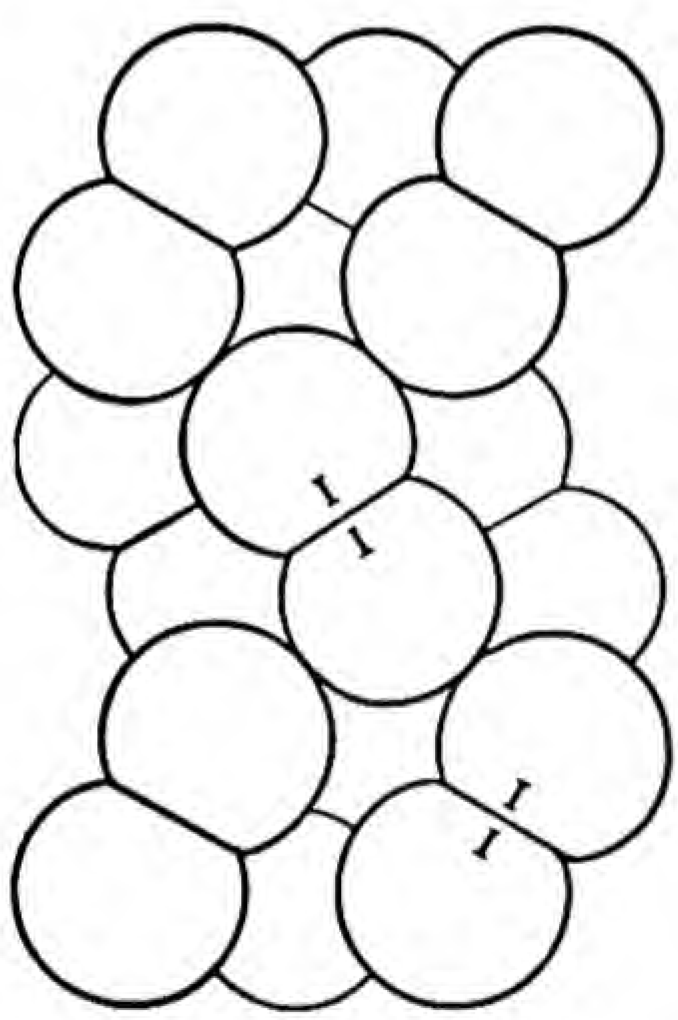


FIG. 51. A crystal of iodine. A typical molecular crystal. Observe the close packing of molecules, I_2.

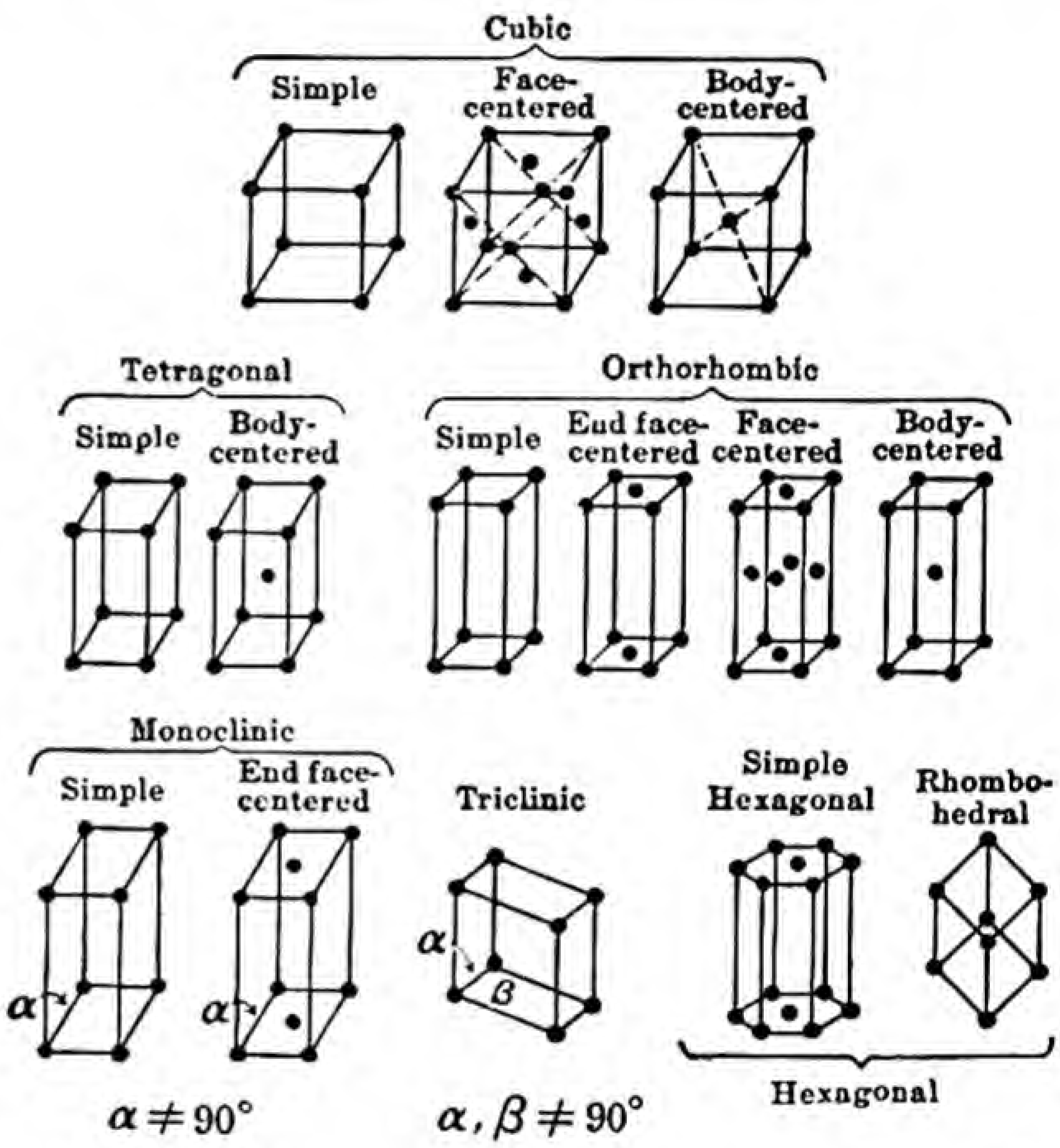


FIG. 52. Fourteen types of unit cells. The rhombohedral unit cell has a special type of 6-fold symmetry.

types of symmetry possessed by crystals, as shown in Fig. 52. Dots in this figure indicate the centers of the atoms which touch, in filling the unit cell.

► 142. Ionic vs. Non-Ionic Crystals

When crystals of the compounds classed as *alkalies* (NaOH, KOH, etc.) and most of those classed as *salts* (NaCl, $KClO_3$, etc.) are melted, the liquid so obtained is found to be a good conductor of electricity. Most other crystals, on being melted, yield liquids that are very poor conductors.

The explanation is that crystals of the alkalies and of most salts are not constructed of ordinary atoms and molecules but of electrically charged atoms or groups of atoms called **ions.** The metals in every such substance are present as positively charged ions (often called *cations*) and the non-metals as negatively charged ions (often called *anions*). Examples:

Sodium hydroxide, NaOH, consists of equal numbers of sodium ions, Na^+, and hydroxyl ions, OH^-.

Sodium chloride, NaCl, consists of equal numbers of sodium ions, Na^+, and chloride ions, Cl^- (Fig. 53).

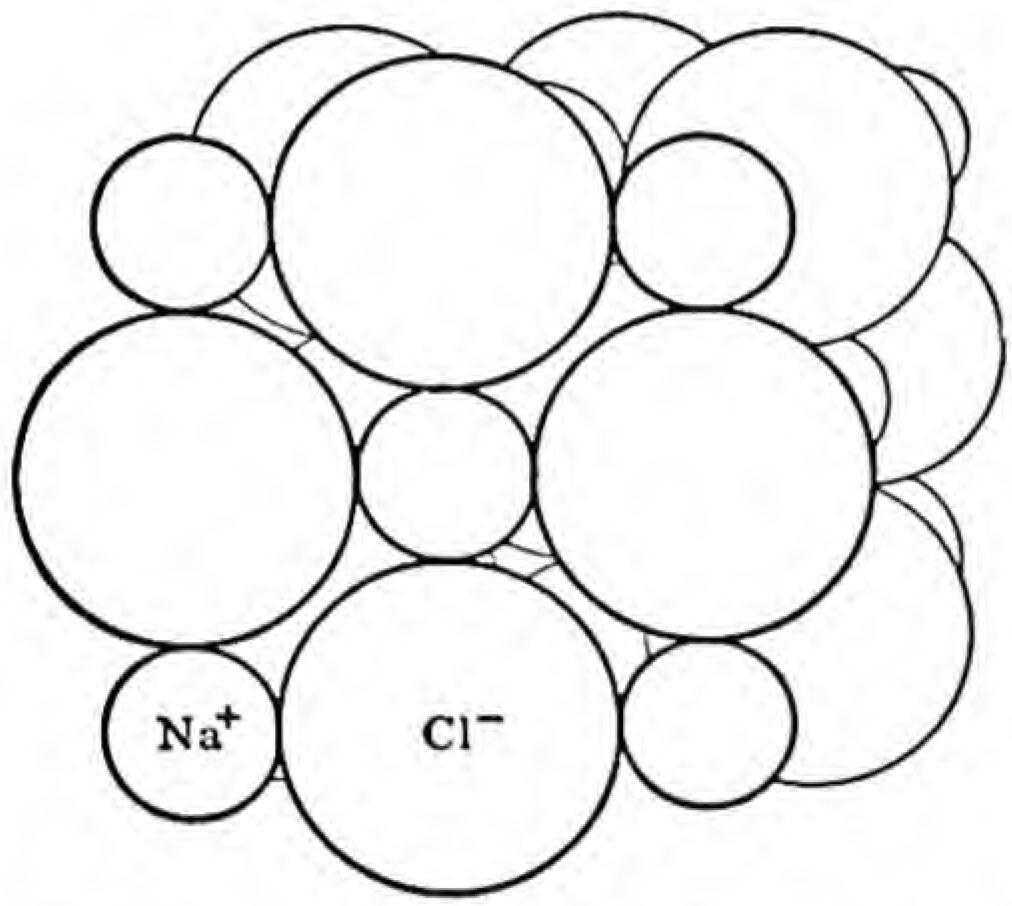


FIG. 53. Showing close packing of ions in a crystal of sodium chloride. Each ion is in contact with six of the opposite kind (face-centered cubic packing).

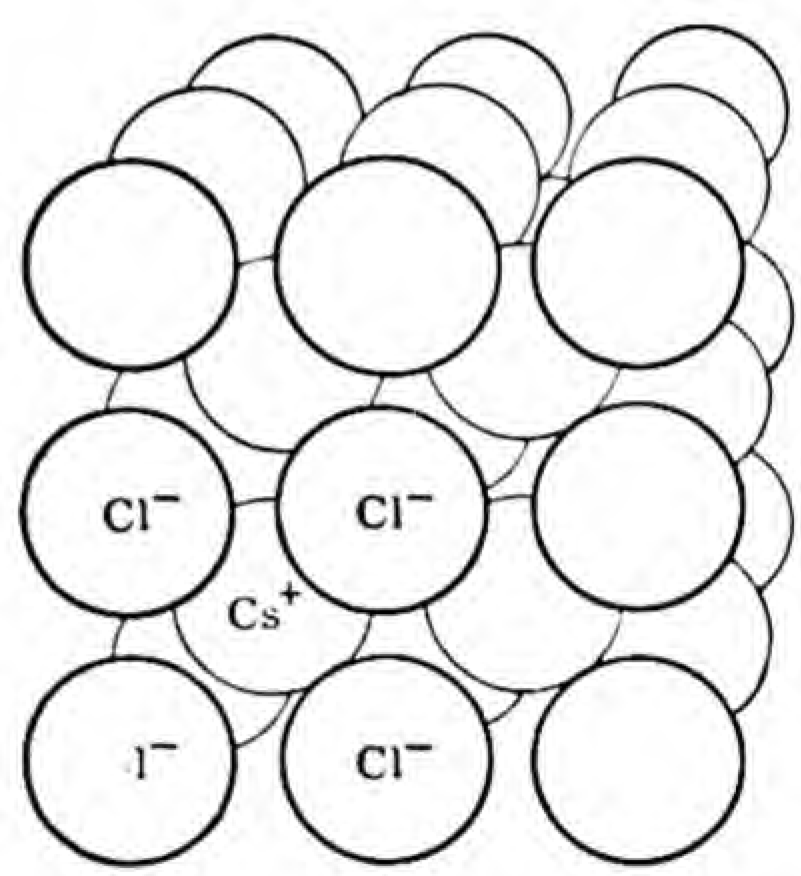


FIG. 54. Showing close packing of ions in a crystal of cesium chloride. Each ion is in contact with eight of the opposite kind (body-centered cubic packing).

Potassium chlorate, $KClO_3$, consists of equal numbers of potassium ions, K^+, and chlorate ions, ClO_3^-.

As long as these substances are in the condition of crystalline solids, the ions that compose them are fixed in definite positions, within the crystal. But when the crystal is melted or dissolved its orderly internal structure is broken down, and its ions acquire nearly complete freedom of motion.

If we now introduce oppositely charged wires (*electrodes*) into the liquid, the two oppositely charged groups of ions move through the liquid in opposite directions, *each ion moving toward the electrode of opposite charge to itself, carrying its own charge of electricity with it.* The ions act somewhat like ferryboats, ferrying the electricity across from one electrode to the other, in a multitude of separate, small charges. So the liquid is found to be a conductor of electricity.

We have emphasized that the crystals of the alkalies and of most salts are composed of ions, rather than of ordinary uncharged atoms and molecules. They are termed *ionic crystals.* Crystals of most other substances, on the contrary (the elements, non-metallic oxides, most classes of organic compounds, most crystalline acids) are non-ionic crystals, for they are composed of ordinary uncharged atoms and molecules, rather than of ions.

► 143. Contrasting Properties of Ionic and Non-Ionic Crystals

The particles within an ionic crystal are held together by strong electrical forces, due to the attraction of oppositely charged neighboring ions. The result is a crystal that is (1) at least moderately strong and hard, (2) difficult to fuse, (3) only slightly soluble in solvents (such as carbon disulfide, CS_2) that happen to be of slight chemical activity,[2] and (4) but slightly volatile. An example is common salt, NaCl. (Ex. 4.)

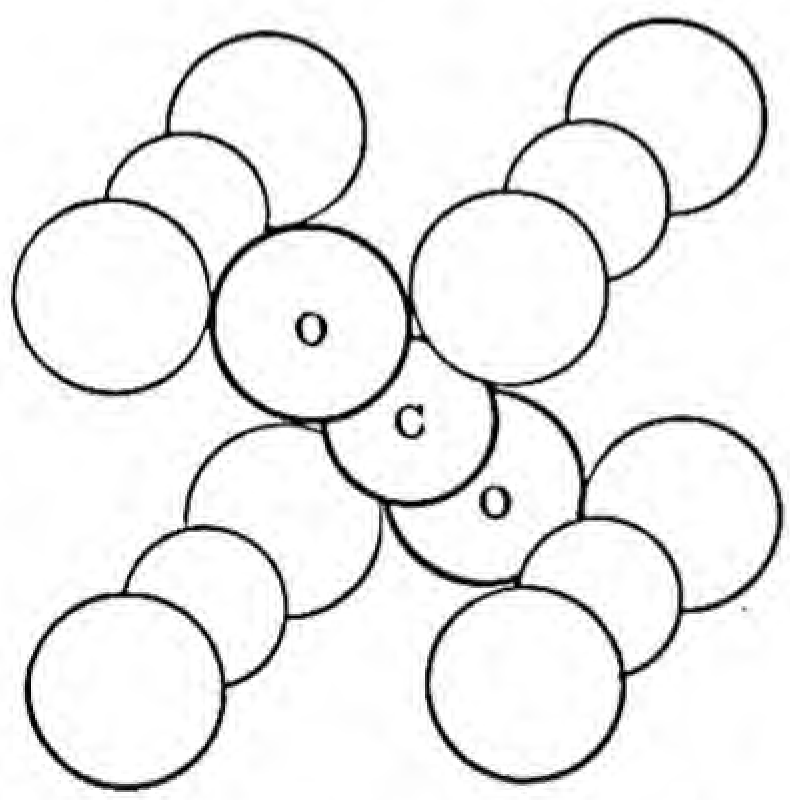


FIG. 55. A crystal of carbon dioxide. Observe how alternate molecules, CO_2, are turned through an angle, to permit much closer packing than could be clearly indicated in this figure.

Non-ionic crystals may roughly be classified in three main structural classes:

1. *Molecular crystals.* The particles composing these are electrically neutral, uncharged molecules. Nevertheless, weak electrical forces do exist between them, for reasons hereafter considered (§ 246). Since these forces are weak, molecular crystals in general (1) are soft and brittle; (2) melt at very low temperatures, (3) dissolve readily in solvents of slight chemical activity (but are frequently insoluble in water), and (4) are readily vaporized.

Examples of molecular crystals are (1) the *non-metallic elements,* such as hydrogen, nitrogen, argon, and sulfur, in the solid state; (2) most *non-metallic oxides;* and (3) many classes of *organic compounds* (compounds of carbon).

A typical molecular crystal is carbon dioxide. In this the uncharged CO_2 molecules that constitute gaseous carbon dioxide are fitted together to make a solid structure (Fig. 55). The bonds within each

[2] A conspicuously *active* solvent (such as water) may combine with ions of an ionic crystal and thus tear down the crystal structure, in brief, may cause the crystal to dissolve, in spite of rather strong internal forces within the crystal (§ 286).

molecule, between each carbon atom and its two neighboring oxygen atoms, are very strong. On the contrary, forces binding each CO_2 molecule to its neighbors within the solid are very weak. No wonder that molecules escape, *ready made*, from the surface of the solid, in other words, that this material *sublimes* (§ 159).

Another example is solid iodine; in each corner of the space lattice of this crystalline solid (Fig. 51, p. 158) is an uncharged double atom, namely, the I_2 molecule, just as in iodine vapor. Solid iodine, too, very readily sublimes.

2. *Metallic crystals* are those of the metallic elements (Na, Mg, Cu, etc.). They are good conductors of heat and electricity, and are often or usually ductile or malleable (§ 491). The reasons for these properties will be sought hereafter. At present we need only note that the electrical conductivity of solid metals is ordinarily very much greater than that of the conducting liquids obtained by melting or dissolving ionic crystals.

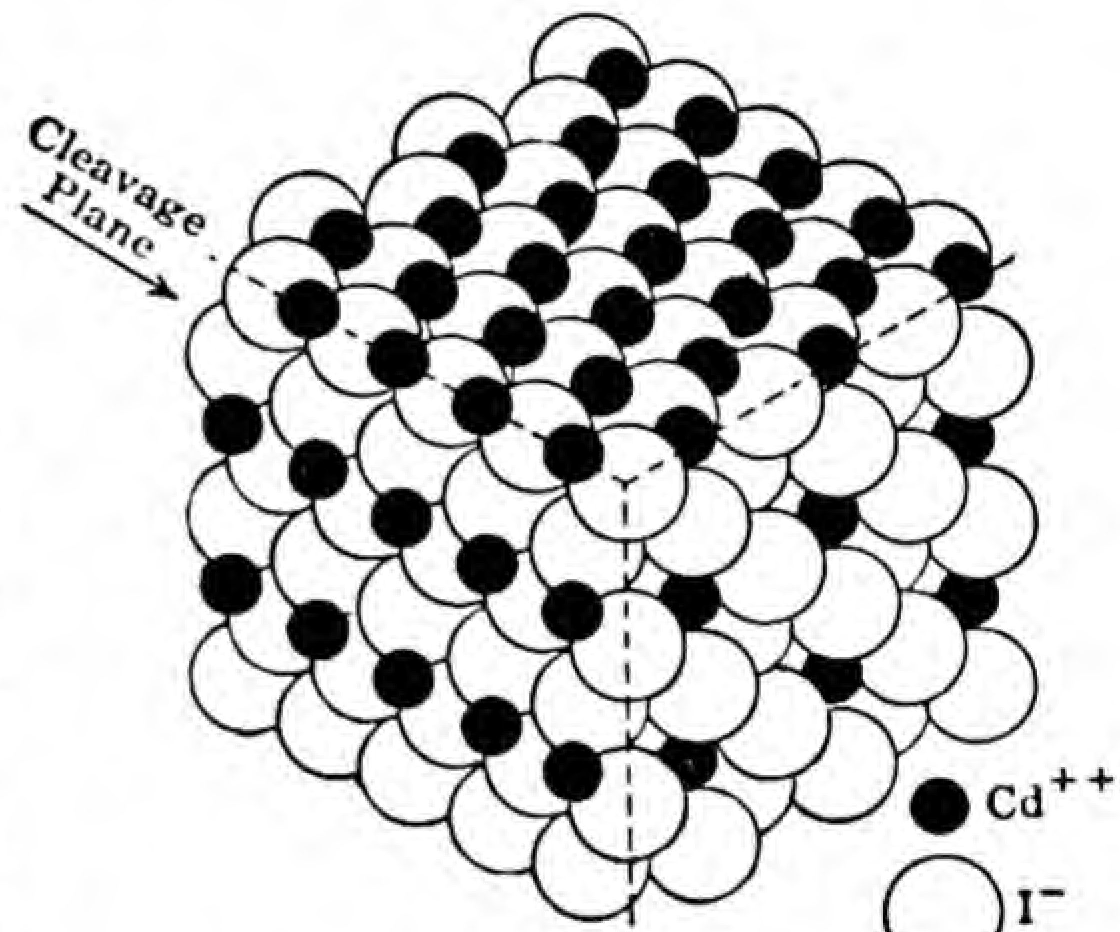


FIG. 56. A layer crystal, CdI_2. Observe that two sheets of iodide ions, I^-, are in contact at the cleavage plane.

3. *Covalent crystals* are those in which the particles are drawn together within the crystal lattice by powerful *magnetic forces*—the same forces, in fact, that bind atoms together in forming molecules. A chain of atoms within the crystal, or a layer of atoms, or even the whole crystal may thus be linked together to form what is in effect a single closely knit molecule of gigantic size. When this process goes to extremes we obtain a crystal with extreme hardness and infusibility. The diamond and silicon carbide, SiC, are examples. More details are given in a later chapter (§ 441).

Layer crystals and *filament crystals* are special types of covalent crystals in which the forces that bind the particles together are strong in certain planes and very weak in others. Such a crystal readily cleaves into thin flakes (mica; iodine; CdI_2, Fig. 56), or into filaments or fibers (asbestos). The different types of ionic and non-ionic crystals really grade imperceptibly into one another, through many intermediate types, some of which will be encountered in later chapters of this book. (Ex. 5, 6.)

144. What Determines Crystal Form?

If the various sorts of particles within a crystal are not markedly different in size, the unit cell, hence the crystal form, is chiefly determined by *the relative numbers of particles* of the different kinds. In *ionic crystals* the relative numbers of particles are determined by the fact that *the total charge on the positive ions must equal the total charge on the negative ions*, in order that the crystal as a whole may be electrically neutral.

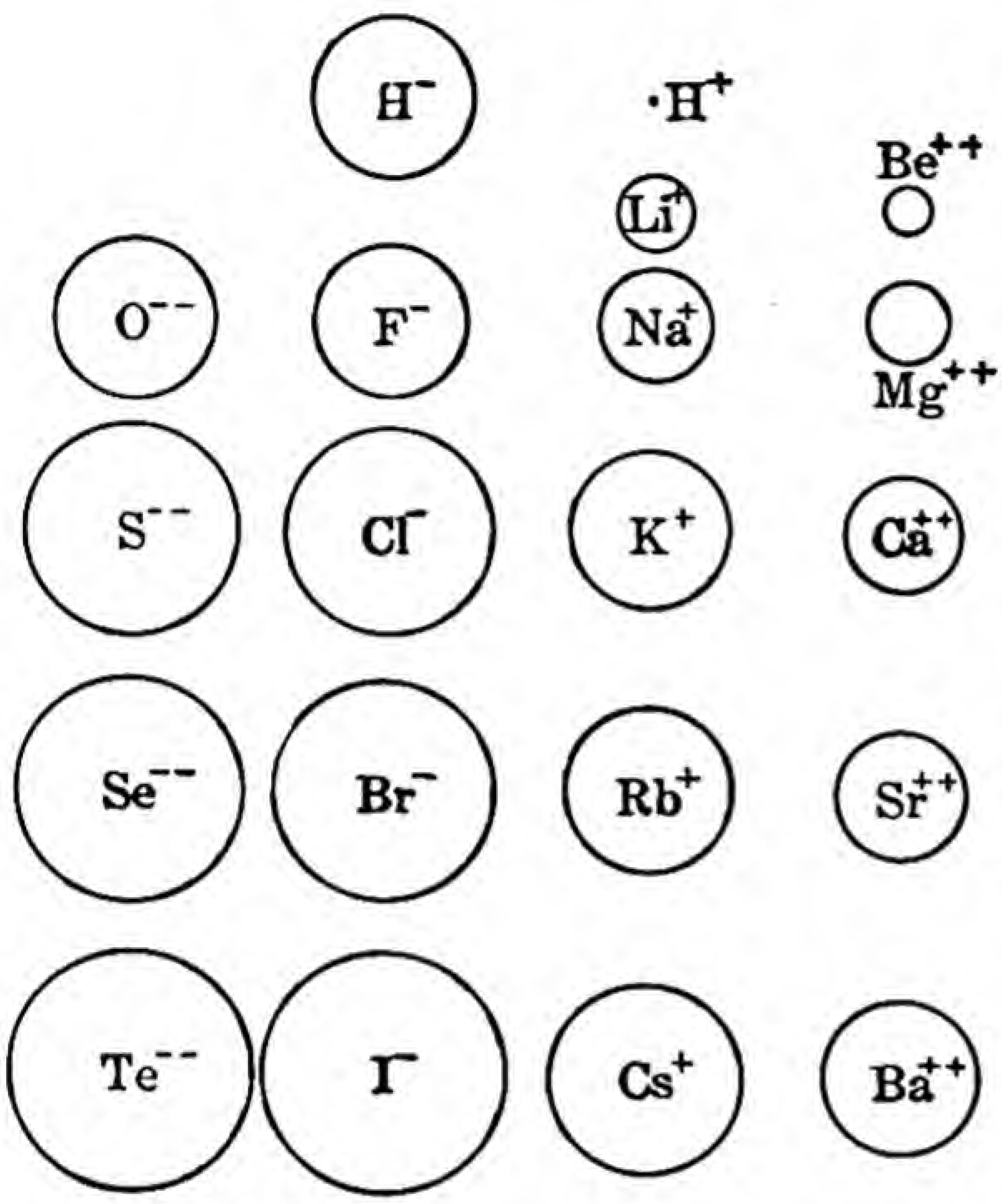


FIG. 57. Relative sizes of a few simple ions. 1 cm = 1.5 Å.

Very simple formulas, such as that of sodium chloride, NaCl, permit the construction of crystals of the highest symmetry, namely, crystals of the *cubic* class; with very complicated formulas, such as that of ferrous sulfate heptahydrate, $FeSO_4 \cdot 7H_2O$, no high degree of symmetry is ordinarily possible, hence the crystal is likely to crystallize in the least symmetrical of the crystal types, namely, the *anorthic* (*triclinic*) class. (Ex. 7.)

If the particles (atoms, molecules, or ions) composing a crystal differ greatly in size, the largest particles will determine which of the fourteen types of unit cells shall be used in constructing the crystal, and hence the form and symmetry of the crystal. Smaller particles are then fitted into the spaces between the larger ones.

X-ray measurements of center-to-center distances within crystals show that even simple *anions*, such as the chloride ion, Cl^-, the oxide ion, O^{--}, and the hydroxide ion, OH^-, are larger than any of the common *cations*. Doubly charged cations (Ca^{++}, Zn^{++}, etc.) are usually smaller than singly charged cations (Na^+, K^+), and those with a triple charge (Fe^{+++}, Al^{+++}), if capable of independent existence, are smaller still (Fig. 57).

With most of the thousands of silicate minerals occurring in nature it is therefore oxygen rather than silicon or the metals that determines the type of symmetry and crystal form. (Ex. 8.)

► 145. Hydrates, Solvates, and Double Salts

When an ionic crystal is dissolved in water, the ions combine with some of the water, to form *hydrated* ions. Then when the solution is evaporated the positive and negative ions are deposited in their appropriate places in a crystal lattice, thus building up a crystal, *and very often carry with them the water with which they happen to be combined.* The result is a crystal that contains a definite amount of chemically combined water, and that consequently may be represented by a definite chemical formula. Such a crystal is called a *hydrate.* Examples are $FeSO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$. (Ex. 14.)

To the question why the water in a hydrate does not evaporate, the answer is: It *does*, if the surrounding air is dry enough. The crystal crumbles to a structureless powder, as the crystal structure is broken down by the removal of the water molecules, since these are often the very particles that lend stability to the crystal and are chiefly responsible for the crystal's taking the form that it does. Such a loss of moisture by a hydrate, in a dry atmosphere, is termed *efflorescence.* The product is sometimes a "lower hydrate," namely, one containing a smaller proportion of water than the original crystalline material, and sometimes a product that is completely *anhydrous* (free from water).

On the contrary, if an ionic crystal is placed in a very moist atmosphere, moisture will condense upon its surface and combine with (*i.e.*, *hydrate*) the surface ions, thus tearing down the crystal lattice, to form a saturated solution. This is *deliquescence.* If the process continues long enough the entire crystal will at length dissolve.

The presence of water in many solid crystals which are apparently dry need be no mystery. *The molecules of water are fitted in between the other molecules or ions of the crystal*, in such a way as to make the crystal stronger or more stable than it otherwise would be. This is as if a mason should attempt to build a wall with rounded stones, all of about the same size. He might discover that the introduction of other stones, of somewhat different size and shape from those first supplied, would greatly strengthen the structure.

Naturally water is not the only substance that may be fitted into a crystal structure, altering its geometrical form and *increasing its stability.* Crystals that are produced by deposition from solutions of benzene, alcohol, and many other solvents may carry definite amounts of these solvents with them into the finished crystal structure. Crystals containing any chemically combined solvent are often called *solvates*, including hydrates as a special class.

Every hydrate has a definite "range of stability" (Fig. 58) *at each temperature, within which it will neither deliquesce nor effloresce.* This range may be expressed either as a range of *vapor pressure* of moisture

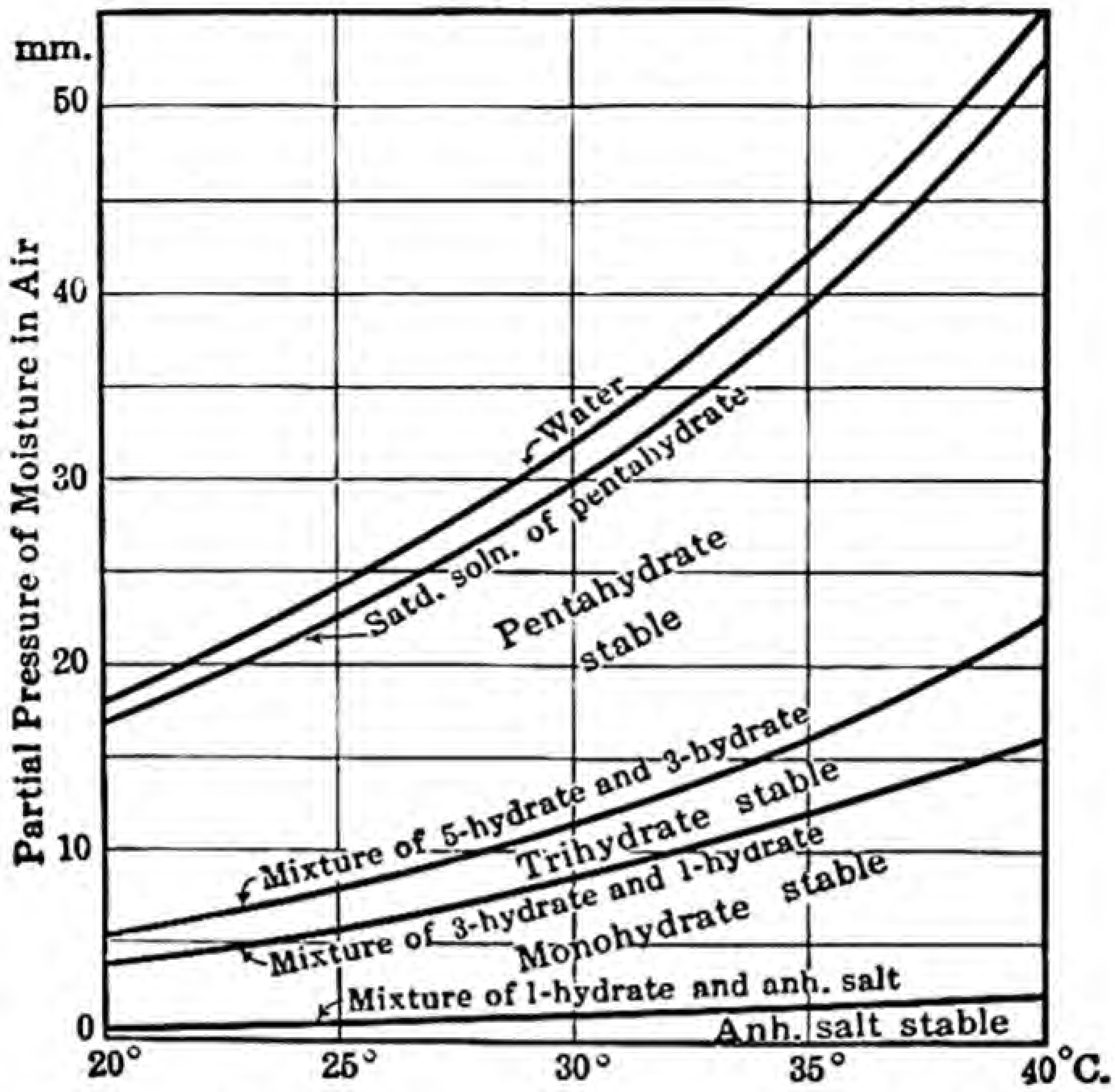


FIG. 58. Stability ranges of different copper sulfate hydrates.

in the air (§ 151) or as a range of *relative humidity* (§ 351). Thus cupric sulfate pentahydrate is stable in air containing moisture corresponding to a vapor pressure of water anywhere between 5.5 and 17 mm, at 20° C. This corresponds to a relative humidity between 31 and 97 per cent (Fig. 58). (Ex. 9, 10.)

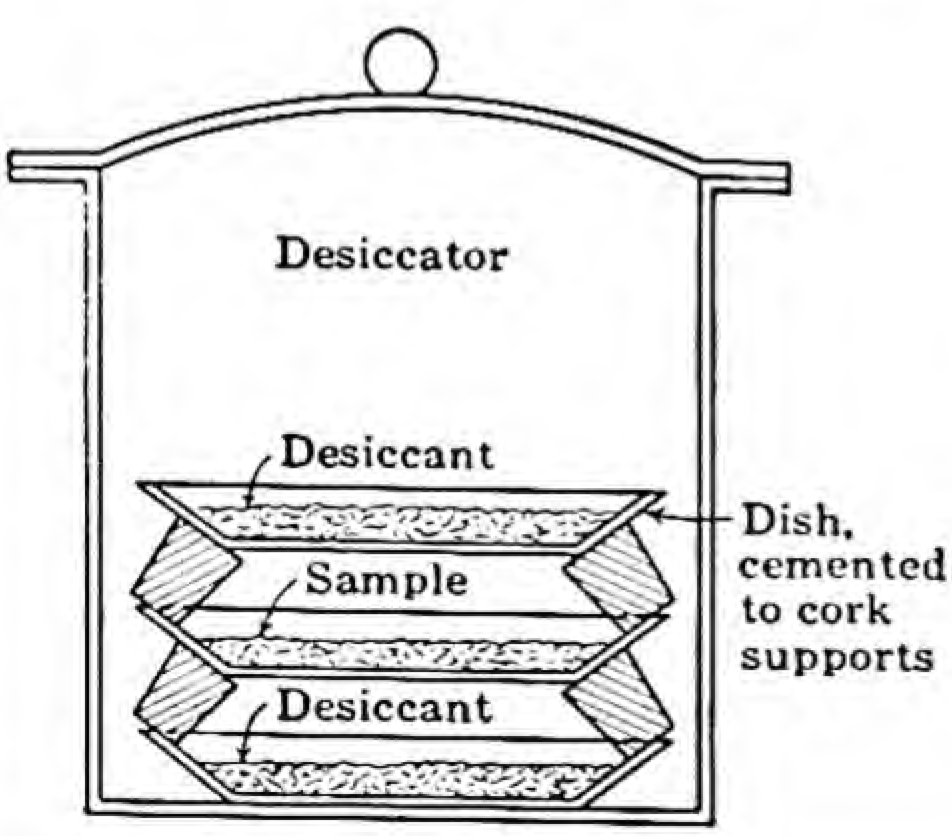


FIG. 59. Drying a hydrate to a definite composition. The desiccant must be a substance which maintains the partial vapor pressure of water vapor, within the desiccator, at some value within the stability range of the hydrate to be prepared.

Sometimes two different salts crystallize together as a *double salt*, in which two different sets of ions are built into the same crystal, to obtain a more stable structure than would otherwise be possible.

Examples are ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, otherwise written $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, and the alums (§ 542), including ordinary "potash alum," $KAl(SO_4)_2 \cdot 12H_2O$. *A double salt contains the same ions as its component salts.* In other words, the formation of a double salt does not involve the formation of new kinds of ions.

146. The Law of Dulong and Petit

The *atomic heat capacity* of any element is its *specific heat times its atomic weight*, in other words the number of calories of heat absorbed by 1 gram atom of the element in being increased in temperature 1 centigrade degree. *At ordinary or slightly elevated temperatures, the atomic heat capacity of most solid crystalline elements is roughly* 6 *to* 6.4. (Law of Dulong and Petit, 1819.) Observe that this applies to *solid elements*, not to non-solids or to compounds.

A century ago this rule was of importance as a means for obtaining *approximate atomic weights*. The specific heat of a solid element (such as sulfur or iron), when multiplied by the atomic weight, was assumed to give 6. And so by dividing 6 by the specific heat of the solid element one might obtain the atomic weight, usually within 5 or 10 per cent. But after 1858 atomic weights were readily deduced by a method of reasoning based on Avogadro's Principle, as outlined in an earlier chapter (§ 33), and the Law of Dulong and Petit lost practical importance. (Ex. 11, 12.)

For us, the chief interest in the Law of Dulong and Petit is in what it reveals concerning the internal structure of crystals. Every atom or ion of a crystalline solid swings back and forth about an equilibrium position. Its *kinetic energy* may be resolved into three parts, corresponding to motion in three directions in space, in other words to three degrees of freedom (§ 120). But the atoms or ions composing a solid, unlike the molecules of an ideal gas, attract one another strongly, and so possess mutual *potential energy*. At the mid-point of its swing the energy of an atom or ion is all kinetic; as it reaches the end of its swing its energy is all potential. For an average particle, the *total energy* is twice the kinetic, hence corresponds to $2 \times 3 = 6$ degrees of freedom, and so (§ 121) to a heat capacity of very nearly 6 calories for each gram atom, as Dulong and Petit observed.

For crystals composed of simple ions (NaCl, for example) the ions act as independent particles in the manner just described, hence the heat capacity of a gram-formula weight (2 gram ions) is roughly 12. Even at room temperature the elements of lowest atomic weight

(Be, B, C) have a much lower atomic heat capacity than the Law of Dulong and Petit predicts, though they conform to the law at higher temperatures.

At very low temperatures, any further lowering of temperature always results in the very rapid decrease of the heat capacity of a crystalline solid.

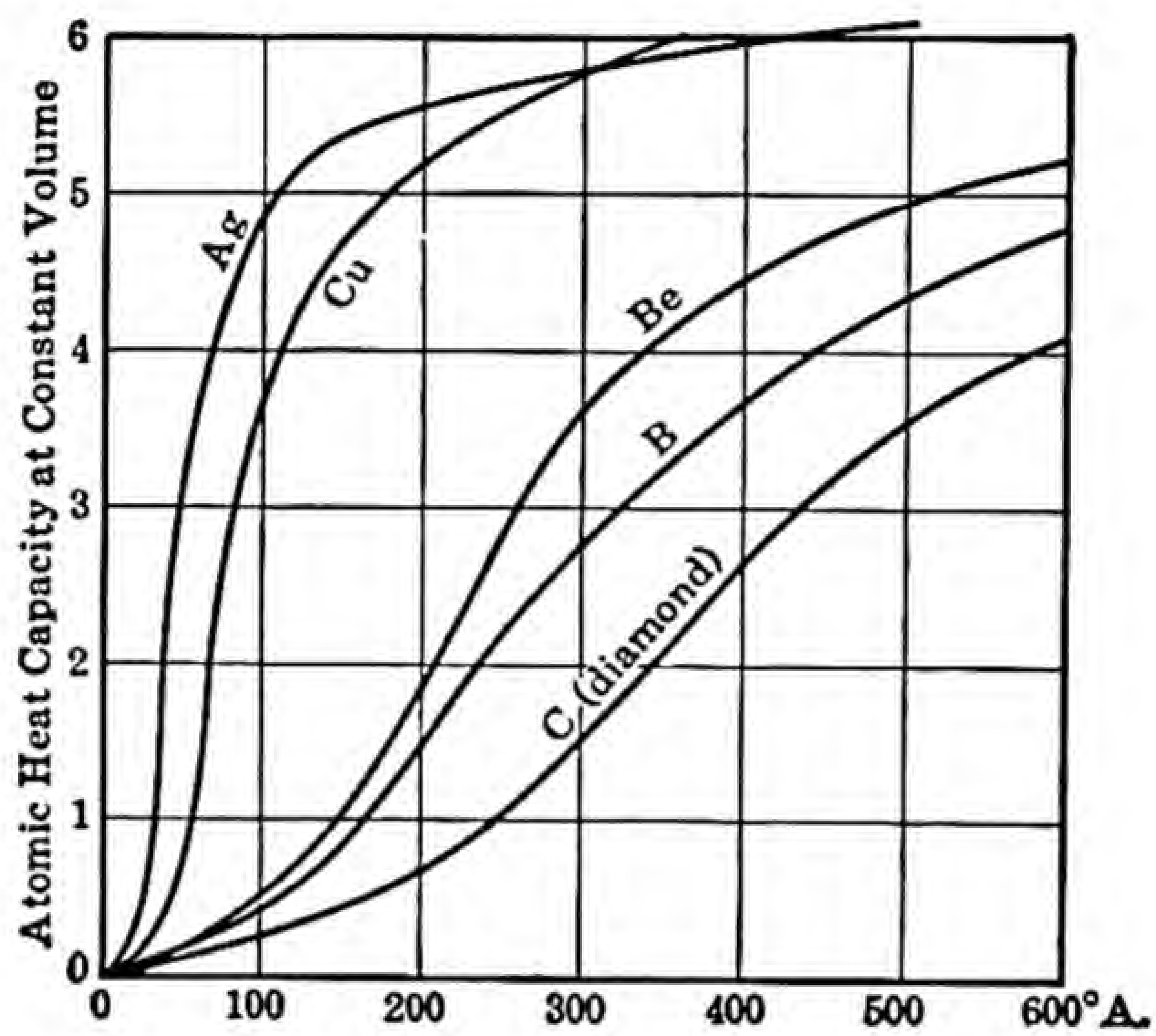


FIG. 60. Atomic heat capacity of several crystalline solids.

The heat capacity of a solid element always approaches zero at absolute zero, as shown in Fig. 60.

147. Crystalline Liquids

Several hundred substances are known which possess the fluidity characteristic of *liquids*, together with some of the properties of *crystals*. Such a substance, at low temperatures, may exist in a truly crystalline condition. As the temperature is raised the material melts sharply to form a turbid liquid (the *liquid crystalline state*). This has the striking property of resolving ordinary light into two separate beams, as many crystals do. These beams are always plane polarized in perpendicular planes (Fig. 61). At a somewhat higher temperature this crystalline liquid suddenly becomes clear. It is then in the ordinary liquid state.

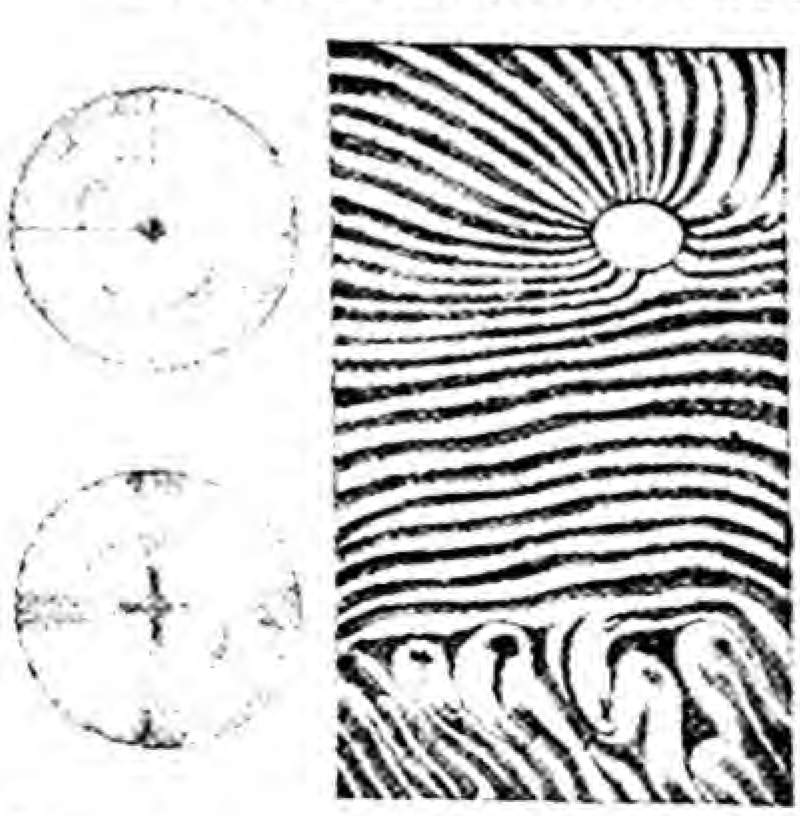


FIG. 61. Droplets and distorted mass of a crystalline liquid, viewed under polarized light, in a microscopic field.

Crystalline liquids (often called *liquid crystals*) may be viewed as crystals that happen to be so weak, in certain directions through the crystal, that they collapse to liquids under the force exerted by their own surface tension. In the collapsed condition they seem to be completely fluid, yet their directional properties indicate that their molecules are still arranged in an orderly manner, to form parallel chains or filaments, or parallel planes that readily slip over one another, like so many glass plates. (Ex. 13, 14.)

148. Summary

We have pictured crystals as being constructed of atoms, molecules, or ions, regularly spaced and arranged with respect to one another. We thus easily explained how crystals come to possess plane surfaces, meeting at definite interfacial angles, why they tend to possess symmetrical forms, why most of them have directional properties, why they melt or decompose at definite temperatures, and why they absorb definite amounts of heat in so doing.

Moreover, we explained the striking differences between ionic and non-ionic crystals by assuming that the former are composed of electrically charged particles and the latter of electrically neutral particles. We accounted for the different shapes that crystals assume by observing that these must depend on the relative members of particles of different kinds, built into the crystal, and on their sizes and shapes.

We next recognized hydrates as crystals formed by the evaporation of solutions in which certain ions are so firmly united with water molecules that some of this water is finally incorporated in the crystal, giving it a different form and more stability than it otherwise would have. Solvates in general and double salts were recognized as similar instances in which two or more substances are jointly incorporated into the structure of a crystal, to give it more stability than it otherwise would have. Finally, we found a simple interpretation of crystalline liquids.

Nevertheless, our explanations have raised a multitude of new questions that clamor for an answer: Where do the ions in ionic crystals acquire their electrical charges? Why do not the oppositely charged ions within any crystal electrically neutralize one another? What is the nature of the forces that unite atom with atom, in forming molecules? Why should metals, even in the solid state, be excellent conductors of electricity, whereas salts ordinarily need to be melted before they will conduct, and even then conduct only moderately well? What

is there about the molecules of certain substances that impels them to form crystalline liquids rather than crystalline solids?

Some of these questions can be dealt with in the next few chapters. Others we must leave for the reader to consider in more advanced courses. This book must finally be brought to an end, though there seems to be no end to the questions that are raised in the process of answering others.

Technical Words

The facts imparted in any course in chemistry may soon be largely forgotten. The important thing is to learn *to think about them.* A by-product of this effort should be sufficient mastery of chemical terminology to enable anyone to do further reading on his own account, wherever chemistry may make contact with his own career or interests. Take time out, now, to review the technical words of this and preceding chapters.

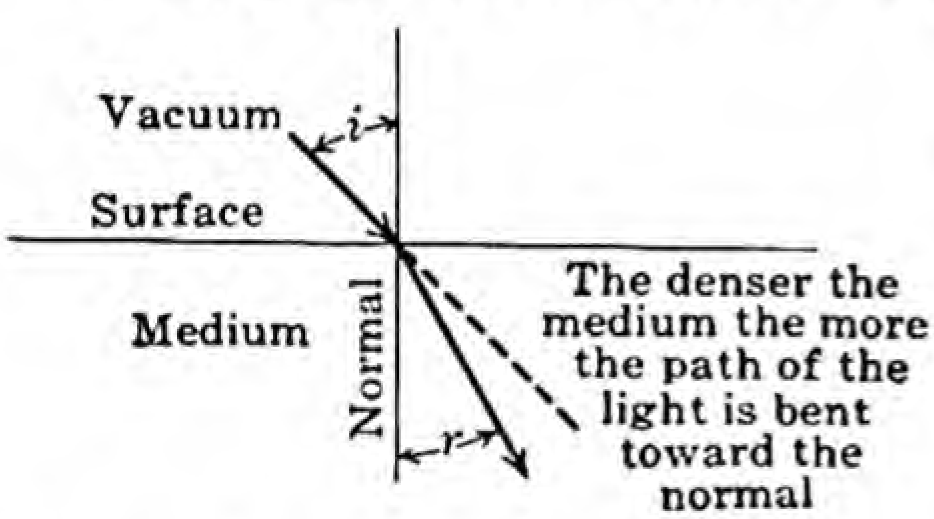
Solid, p. 150. **Rigidity,** p. 150. **Hardness,** p. 150.

Plastic solid, p. 150. **Amorphous solid,** p. 151. **Crystalline solid,** p. 151.

Cleavage, p. 153. **Directional properties,** p. 152.

Interfacial angle—the angle between two faces of a crystal.

Index of refraction—a measure of the amount to which light is **refracted** or bent aside, in entering a given material from a vacuum. It is $\frac{\sin i}{\sin r}$ in the annexed sketch. The index of refraction is also the ratio of the velocity of light in a vacuum to its velocity in the given material.



Doubly refracting, p. 152.

Interatomic distance—the center-to-center distance between nearest neighboring atoms, in a molecule, ion, or crystal.

Symmetrical—possessing a regular internal arrangement or external form, in which all points occur in pairs, at equal distances on opposite sides of a *center, axis, or plane of symmetry.*

Axis of symmetry—an imaginary line, passing through a solid, such that when the solid revolves about it the same external appearance and internal disposition of parts will occur repeatedly, in the course of a single revolution.

Ion, p. 159. **Cation,** p. 159. **Anion,** p. 159.

Ionic and non-ionic crystals, p. 160.

Molecular, metallic, and covalent crystals—the three chief kinds of non-ionic crystals, pp. 160–161.

Layer crystals—crystals in which atoms of different kinds occur in alternate layers.

Filament crystals or **fiber crystals**—crystals in which the atoms are linked in chains or filaments. Bundles of such filaments may constitute a fiber.

Hydrous—combined with an *indefinite* or *variable* amount of water.

Hydrate (n.)—a crystalline substance containing a *definite* proportion of chemically combined water.

Hydrate (v.)—to cause to combine with a definite proportion of water.

Water of hydration—the water contained in a hydrate.

Efflorescence, deliquescence, p. 163.

Double salt, p. 164. **Crystalline liquid,** p. 167.

Organic compound—any compound of carbon (usually excluding the oxides of carbon, carbonic acid, and the carbonates).

Summary

► § 134. Characteristics of solids. What is meant by hardness. Arbitrary scale of hardness. How hardness is determined.

Name given to solids that may be shaped by pressure.

Two kinds of strength. Solids conspicuous for each kind.

► § 135. Two characteristics of crystalline solids. Why crystalline solids sometimes appear to be amorphous. Term applied to brittle, glassy solids.

▷ § 136. A sketch and description of a method by which the melting point of a solid may be determined. How the conclusion from such a test may be confirmed by testing a mixture.

► § 137. What we mean by directional properties. Examples. What we mean by index of refraction. What are doubly refracting crystals.

What we mean by cleavage. Examples.

§ 138. A statement of the law of rational indices for crystal faces. What happens when a crystal grows by deposition from a solution in which impurities hinder deposition on certain faces.

► § 139. How faces having different slopes may be generated by removing bricks from a regularly stacked pile of bricks.

► § 140. How a beam of X-rays may be used to determine the arrangement of particles within crystals. Accuracy with which center-to-center distances between atoms have been measured.

§ 141. What we mean by an axis of symmetry. Different axes in a cube.

How many classes of crystals are found, when they are classified according to their external symmetry.

What is meant by unit cell. How many different types exist.

► § 142. Explanation of the manner in which certain liquids conduct an electric current. A name given to electrically charged atoms or groups of atoms.

Why a solid ionic crystal is a poor conductor, though the liquid produced by melting or dissolving it is a good conductor.

► § 143. Four particulars in which ionic crystals differ sharply from molecular crystals. General properties that distinguish three different classes of non-ionic crystals. Names given two intermediate classes.

§ 144. What determines the relative numbers of ions of each kind within an ionic crystal. How increasing complexity of a chemical formula is likely to affect the crystalline form of the corresponding material.

Whether the shape of a crystal is determined by its largest or by its smallest particles, in instances in which there are marked differences in size. Which common ions are largest. How the charge on a metallic ion affects its size.

► § 145. What happens to the ions of an ionic crystal when the crystal is dissolved in water. A name given to a crystal that contains a definite amount of chemically combined water.

Conditions under which a hydrate will lose water. Name given this process.

Conditions under which a hydrate, exposed to moist air, will liquefy. Name given this process.

Name given to a crystal that contains a definite amount of a chemically combined solvent.

Reason why solvent molecules or two different sets of ions are sometimes included in a crystal.

§ 146. Statement of the Law of Dulong and Petit. What happens to the heat capacity of solids at very low temperatures.

§ 147. How a crystalline liquid differs in some easily observable properties from ordinary liquids. The internal structure of crystalline liquids.

Exercises

1. What are the interfacial angles, in degrees, between the different faces of the hexagonal prism shown in Fig. 50?

2. If we were constructing a crystal model of cubical blocks, would the finished crystal necessarily be a cube? Explain fully.

3. What type of symmetry is ordinarily possessed by a starfish? Is this type observed with crystals?

4. The electrical conductivity of fused sodium chloride is almost ten million times that of the chemically equivalent amount of fused aluminum chloride. What conclusion may be drawn?

5. What type of crystal structure would you assign to solid camphor from the fact that it readily vaporizes?

6. Graphite is a layer crystal which is a good conductor of electricity, but soft and weak. Between which main classes of crystals would you place it, as an intermediate form?

7. Which would you expect to crystallize in crystals of the higher symmetry, potassium chloride, KCl, or potassium chlorate, $KClO_3$? Explain why.

8. A popular lecturer described mica (§ 484) as consisting of "oxygen sheets, interlayered with positive ions." Just what did he mean?

9. In copper sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$, what is the total gram-formula weight (§ 115), including the water of hydration? What is the total formula weight of the indicated five molecules of water? Then what fraction and what percentage of the total weight of the hydrate is water? 250, 900, 360

10. The vapor pressure of water at 20°C is 17.53 mm. Sodium bromide dihydrate, $NaBr \cdot 2H_2O$, is stable in an atmosphere having a relative humidity anywhere between 43 and 66 per cent. What is the actual vapor pressure of moisture corresponding to each limit of the range of stability of this hydrate? 754, 116

11. The specific heat of solid sulfur at room temperature is approximately 0.18. From this and the atomic weight of sulfur calculate its atomic heat capacity. 577

12. From the observed specific heat of vanadium, 0.115, calculate its approximate atomic weight. 520

13. If crystalline liquids have the structure indicated in the text, do you imagine that their viscosity will vary with the direction in which they are made to flow? Explain.

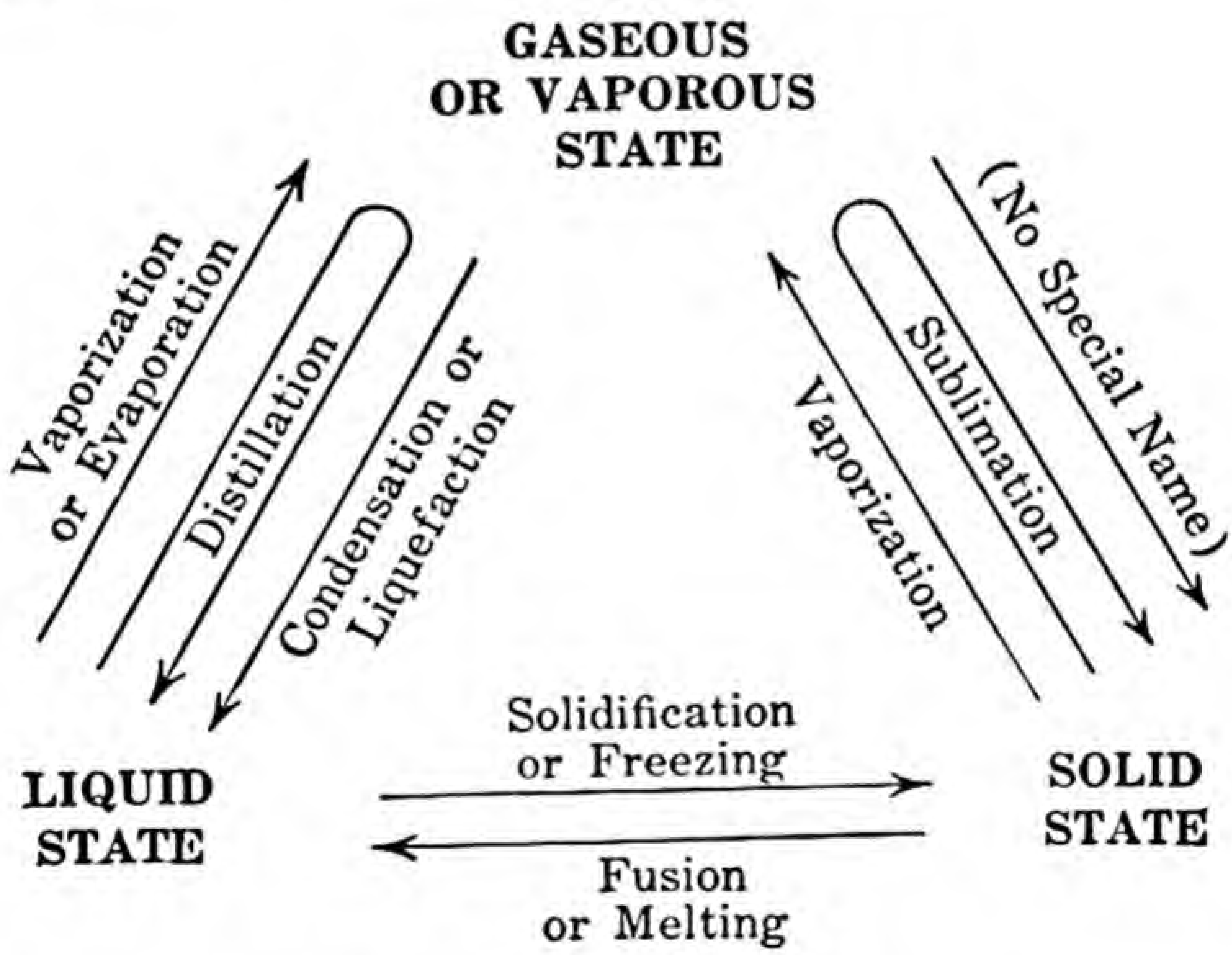
14. A crystalline powder has well-defined X-ray patterns below a certain temperature, but patterns of a different sort above that temperature. What conclusion may be drawn?

Chapter 12

CHANGES OF STATE

► 149. Names for Changes of State

Special names, here summarized in a diagram, have been given to the processes in which each of the three states of matter is converted into the others:



Observe that the word *vaporization* refers to the production of a vapor, from either a liquid or a solid. *Distillation* and *sublimation* are double processes, in which a material is first vaporized, then recondensed to liquid or solid, respectively.

► 150. Evaporation

Every liquid that is perceptibly volatile will still evaporate, though very slowly, at temperatures far below its boiling point. This fact convinces us that we were right in our previous conclusion (§ 122) that the molecules of a liquid, at any given temperature, do not all have the

same speed. If they did, no evaporation would take place below a definite temperature. When this temperature was reached, all the molecules of the liquid would possess sufficient energy to escape into the vapor phase, and evaporation would take place all at once.

Actually, *at any given temperature, only molecules possessing more than the average kinetic energy are able to break through the surface film and escape.* All the rest are turned back. As the temperature is raised a larger and larger proportion of the molecules come to possess sufficient energy to escape. Increasing temperature therefore rapidly increases the rate of evaporation.

Figure 62 is intended to show some of the details concerned in evaporation. Molecules, from below, arriving at the surface layer, are usually simply turned back (as at *a* and *b*). But now and then a molecule, moving upward from below, arrives at the surface with sufficient energy to burst through and enter the vapor space above. Even then it may at once be dragged back into the liquid, by collision with molecules of vapor or by the pull of the molecules beneath it (as at *c* and *d*); but in other cases it makes good its escape and goes wandering off through the space above (as at *e*). It is then a molecule of vapor.

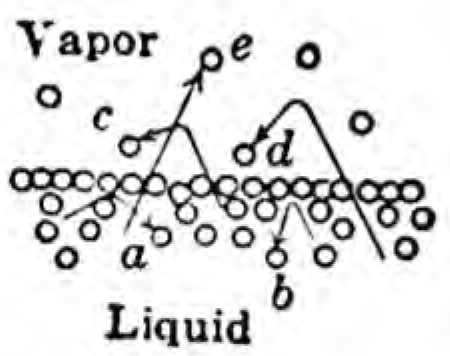


FIG. 62.

Increased surface, of course, offers increased opportunity for the escape of molecules into the vapor phase and hence increases the rate of evaporation. *Blowing a current of air over the surface* removes the molecules of vapor before they have an opportunity to return to the liquid, hence increases the net rate of evaporation. A liquid evaporates more rapidly into a *partial vacuum* than into air, obviously because the vapor molecules, if air were present, would frequently collide with the molecules of air, and be reflected back into the liquid. (Ex. 1, 2.)

► 151. Vapor Pressure

If a volatile liquid (water, for example, or ether) is permitted to evaporate in a closed vessel, the vapor escaping from the liquid into the space above the liquid will always set up a pressure, which may be registered by the displacement of mercury (or some other non-volatile liquid) in a U-shaped tube or gage (Fig. 63). This pressure slowly increases as the vapor accumulates, until at length the space above the liquid (perhaps originally filled with air) has taken up all the vapor that it can *acquire* and *hold* at that temperature. The space above the liquid (or the air that it contains) is then said to be *saturated* with vapor.

The pressure set up by the escaping vapor then ceases to increase, and *remains constant.* This is because a condition of *equilibrium* is then reached between evaporation and recondensation. In other words, when a certain number of molecules of vapor have accumulated above the liquid, new molecules evaporate into that space just as fast as others leave it and return to the liquid.

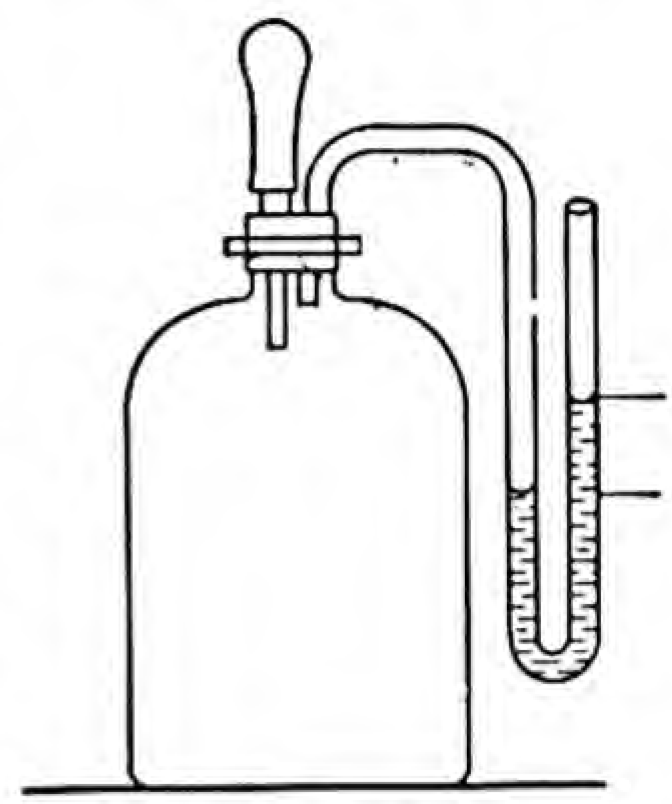


FIG. 63.

The number of molecules of vapor in the space above the liquid thereafter remains constant. By their bombardment of the walls of the vessel they set up a definite constant *vapor pressure,* which depends on the temperature and on the nature of the liquid, but does not depend on the quantity of liquid (provided that there is at least enough of it to saturate the space above it with vapor). (Ex. 3.)

If the space above a liquid contains air, evaporation takes place more slowly than it does into a vacuum; but the same amount of liquid will evaporate and the same vapor pressure will be observed in the end, provided that the temperature is the same in both cases.

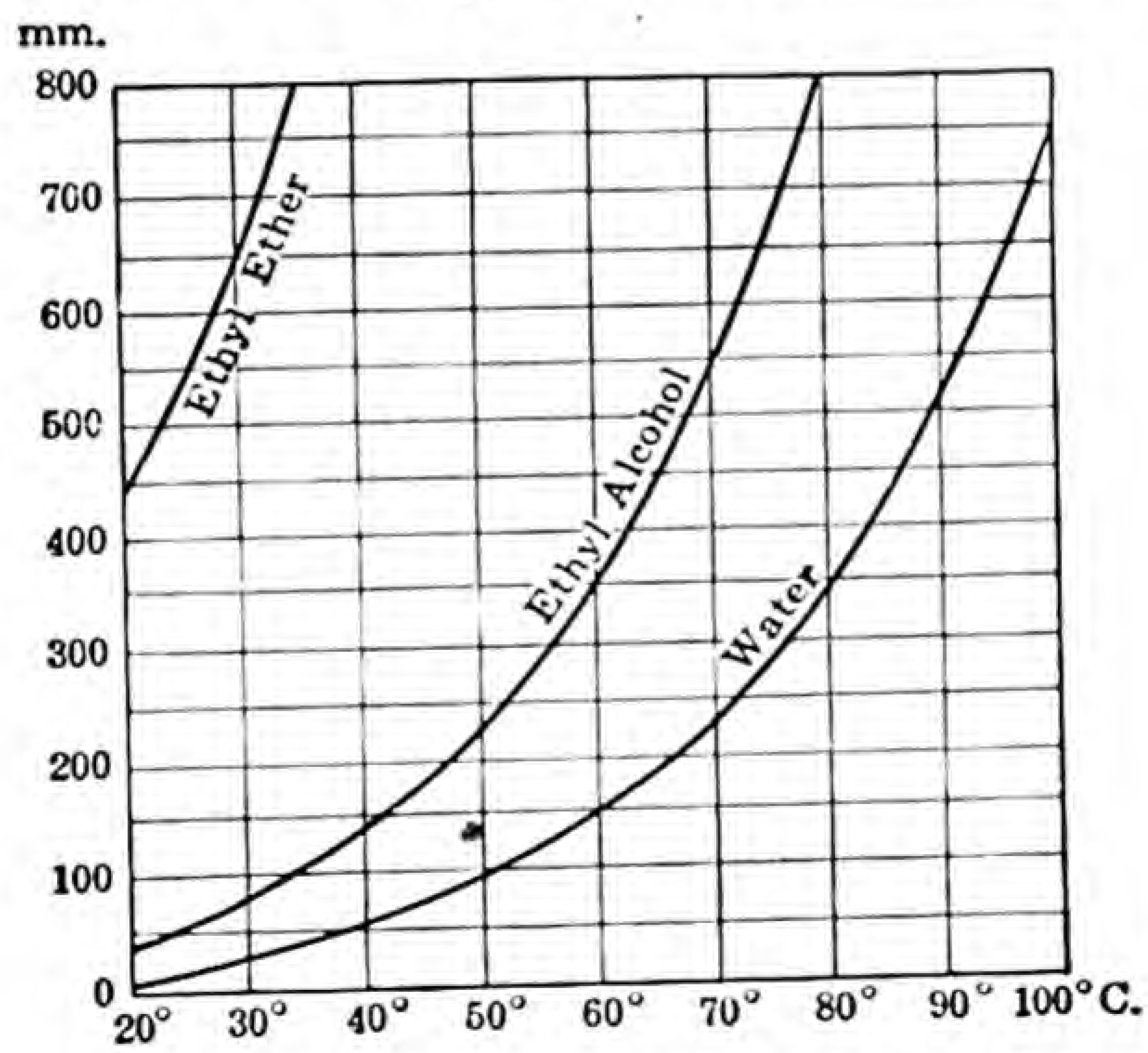


FIG. 64. Vapor-pressure curves.

Different liquids differ greatly in volatility. The more volatile a liquid—that is, the more readily it evaporates—the greater is its vapor pressure at any given temperature. The vapor pressure of a liquid always increases as its temperature is increased, slowly at first, then more and more rapidly, as shown in Fig. 64, for three different

liquids. The vapor pressure is here given in *millimeters of mercury;* in other words, it indicates the difference in level that would be maintained by that pressure in the two arms of a U-tube (Fig. 63) containing mercury.

► 152. Boiling

At low or moderate temperatures the evaporation of a liquid proceeds only as fast as vapor escaping from the surface of the liquid into the surrounding air can be carried away by chance currents of air. In a nearly closed flask or in a stagnant atmosphere evaporation is extremely slow. But if the liquid is *heated* the pressure of the escaping vapor steadily increases, until at last a temperature is reached at which the vapor pressure, *exerted upward*, becomes equal to or slightly greater than the opposing pressure, directed *downward* upon the surface of the liquid, caused by the weight of the overlying atmosphere (about 14.7 pounds per square inch, or 1033 grams per square centimeter, at sea level, corresponding to a barometric pressure of 760 mm of mercury), and measured by a barometer (Fig. 65). The escaping vapor can then *push back* the atmosphere and even slight depths of overlying *liquid*—can shove these back bodily—and so can escape freely, not merely from the surface of the liquid but even by forming bubbles at some distance beneath the surface. These bubbles rise rapidly to the surface, and we say that the liquid boils. Evaporation, thereafter, need not wait for vapor already produced to be carried away by diffusion or by chance currents of air.

FIG. 65.

The temperature at which boiling occurs is called the *boiling point* of the liquid, under the specified pressure. Unless otherwise indicated, the boiling point of a liquid is assumed to be under a pressure of 1 atmosphere (760 mm). From a table of vapor pressures or a vapor-pressure curve (Fig. 64) we may readily determine the boiling point of any given liquid, merely by noting at what temperature the vapor pressure reaches 760 mm. (Ex. 4.)

► 153. Boiling under Reduced or Increased Pressure

The external pressure over a liquid, due to the weight of the atmosphere pressing down upon the liquid, may be reduced with an air

pump, or by transporting the liquid to the top of a high mountain. The temperature then need not rise so high before the pressure set up by the escaping vapor will equal or slightly exceed the external pressure, and hence result in the atmosphere's being pushed back bodily. In brief, *lowering the external pressure will lower the boiling point of a liquid.*

Milk, sugar syrup, and many other materials which would be injured if heated to the temperatures needed to boil them under ordinary atmospheric pressure may be concentrated or evaporated completely in a partial vacuum, in other words *under reduced pressure,* at relatively low temperatures, in vacuum evaporators. Milk powder is often produced by spraying milk into a warm chamber from which air is removed by a powerful pump, and in which evaporation consequently takes place almost instantly. This process is sometimes called "spray drying."

When heating a liquid in a closed, strong-walled vessel called a *pressure cooker*, or *autoclave*, the free escape of vapor that constitutes boiling is prevented. The most that can then happen (unless the safety valve opens) is the quiet evaporation of some of the liquid and the accumulation of the vapor, under pressure, within the autoclave. We thus proceed when it is desired to heat a liquid above the temperature at which it would ordinarily boil. Glucose syrup, for example, is prepared by heating starch in autoclaves in the presence of a little hydrochloric acid. Bacteriologists regularly sterilize their culture media in autoclaves. Vegetables that are sufficiently cooked only by a long period of heating at the ordinary boiling point of water are finished in a shorter time in a pressure cooker, because of the higher temperature attainable. (Ex. 5, 6.)

► 154. Heating a Liquid in a Closed Space

We have just observed that when a liquid is heated in a strong-walled, closed vessel it cannot boil, for the simple reason that the escaping vapor cannot displace the vapor already accumulated and the air present within the vessel from the beginning. Yet more and more vapor does evaporate into the space above the liquid, as the temperature is raised. Thus the vapor gradually becomes more and more dense, whereas the unevaporated liquid, since it *expands* as it is heated, becomes less and less dense.

If we keep on raising the temperature and the vessel is strong enough to hold the accumulating vapor, liquid and vapor finally acquire the same density, in fact become identical in all their properties. Liquid and vapor are then indistinguishable, and intermingle

freely, hence the surface that separates the liquid from its vapor suddenly disappears. The temperature at which this happens, for any given liquid, is called its *critical temperature.* It is the temperature above which a gas cannot be liquefied by any pressure, however great.

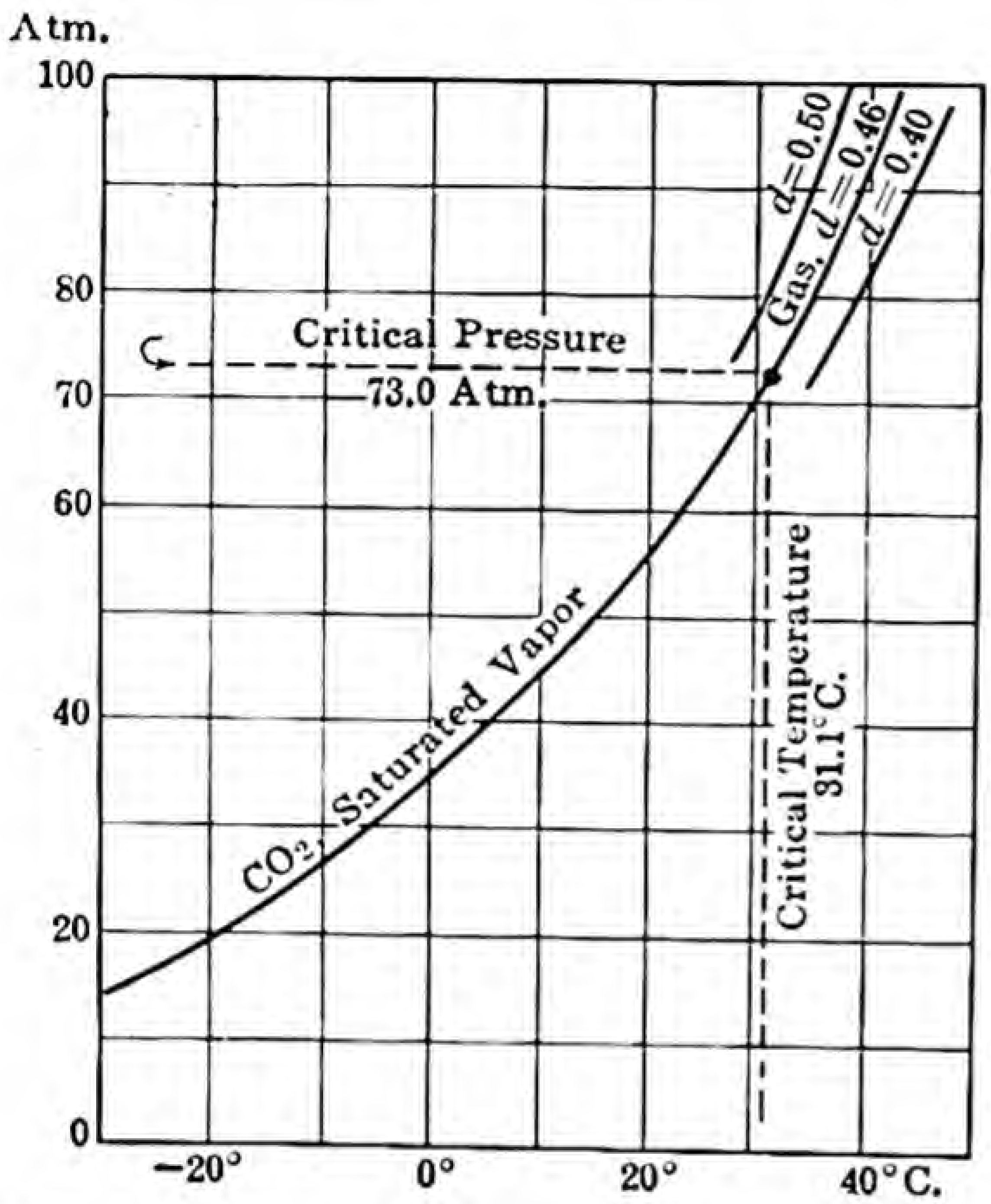


FIG. 66. Vapor pressure of liquid carbon dioxide.

It is only below its critical temperature that a gas may properly be referred to as a vapor. The *critical pressure* of a liquid is its vapor pressure at the critical temperature.

There is no sudden increase of pressure at the critical temperature. As the temperature of a liquid is increased the pressure steadily increases, too, up to and beyond the critical temperature. Below the critical temperature this pressure is entitled to be called a *vapor pressure,* since it has a definite value at each temperature, regardless of how much liquid there is, provided that some liquid remains unevaporated. Above the critical temperature, we no longer have a vapor but a *gas,* which will exert a pressure that is determined by *how much gas,* at the given temperature, is contained in the vessel. All this is clearly shown in Fig. 66. (Ex. 7.)

▶ 155. Heat of Vaporization

Everyone who has had to face a wind in wet clothing knows that *rapid evaporation causes heat to disappear, and hence results in cooling.* This principle has been in use since prehistoric times, in cooling water in hot climates by placing it in porous earthenware vessels exposed to a breeze. A portion of the water passes through the porous walls and evaporates from the surface of the vessels, thereby cooling what remains. If evaporation is made very rapid, by permitting water to evaporate into a vacuum created by a powerful vacuum pump, heat may disappear so rapidly in this process that the water which remains is actually frozen solid!

Evaporation causes heat to disappear because energy must be expended (1) in overcoming the attraction of the molecules of the

liquid for one another, as the liquid evaporates, and (2) in pushing back the atmosphere. Only the most swiftly moving molecules possess sufficient energy to escape. Their escape decreases the average energy of the molecules that remain; in other words, it lowers the temperature of the unevaporated liquid.

The *heat of vaporization* (or *heat of evaporation*) of a liquid is the total heat in calories that disappears (in the two ways just mentioned) at any given temperature in evaporating 1 gram of the liquid, when the external pressure is 1 atmosphere. When a vapor condenses, the energy that it absorbed in being vaporized is again released as heat. The heat of vaporization of a liquid decreases steadily with increasing temperature and becomes zero at the critical temperature.

Water has the greatest heat of vaporization of any known liquid (539.6 calories per gram, at 100°C). This is due to its being an *associated* liquid, as explained in § 123. It consequently absorbs more heat from the surroundings on being vaporized and releases more heat on being condensed than an equal weight of any other substance. Steam-heating systems transfer a maximum amount of heat with a minimum weight of condensed material returned to the boilers. This property of water is an advantage when steam is used as a source of motive power in steam boilers. Yet water suffers from the serious disadvantage of producing *inconveniently high pressures* at high temperatures. A liquid with a higher boiling point would be better in this respect. Several have been proposed, for example, a mixture of diphenyl and diphenyl oxide, two organic substances that are stable at boiler temperatures.

► 156. Refrigeration

If the energy needed for the evaporation of a liquid is furnished by the part of the liquid that remains unevaporated, the temperature of that part will be lowered. Liquefied gases, such as ammonia and carbon dioxide, absorb less heat than water does when they evaporate, that is, they have a lower heat of evaporation, but make up for this by evaporating at lower temperatures. One need only open a valve at the top of a cylinder of liquefied gas to note that the liquid actually boils at a point well below room temperature.

The first liquefied gas to be used as a refrigerant on a large scale was ammonia. At the present time, thousands of installations use liquid ammonia for refrigeration or for the manufacture of ice. In the United States, more than 40,000,000 tons of ice are manufactured, annually, using liquid ammonia as a refrigerant. Observe how manufacture of ice, in Fig. 67, is combined with cold storage. (Ex. 8.)

Small industrial installations sometimes employ liquid carbon dioxide as a refrigerant instead of ammonia. As much heat disappears in the direct vaporization of solid carbon dioxide as in the successive

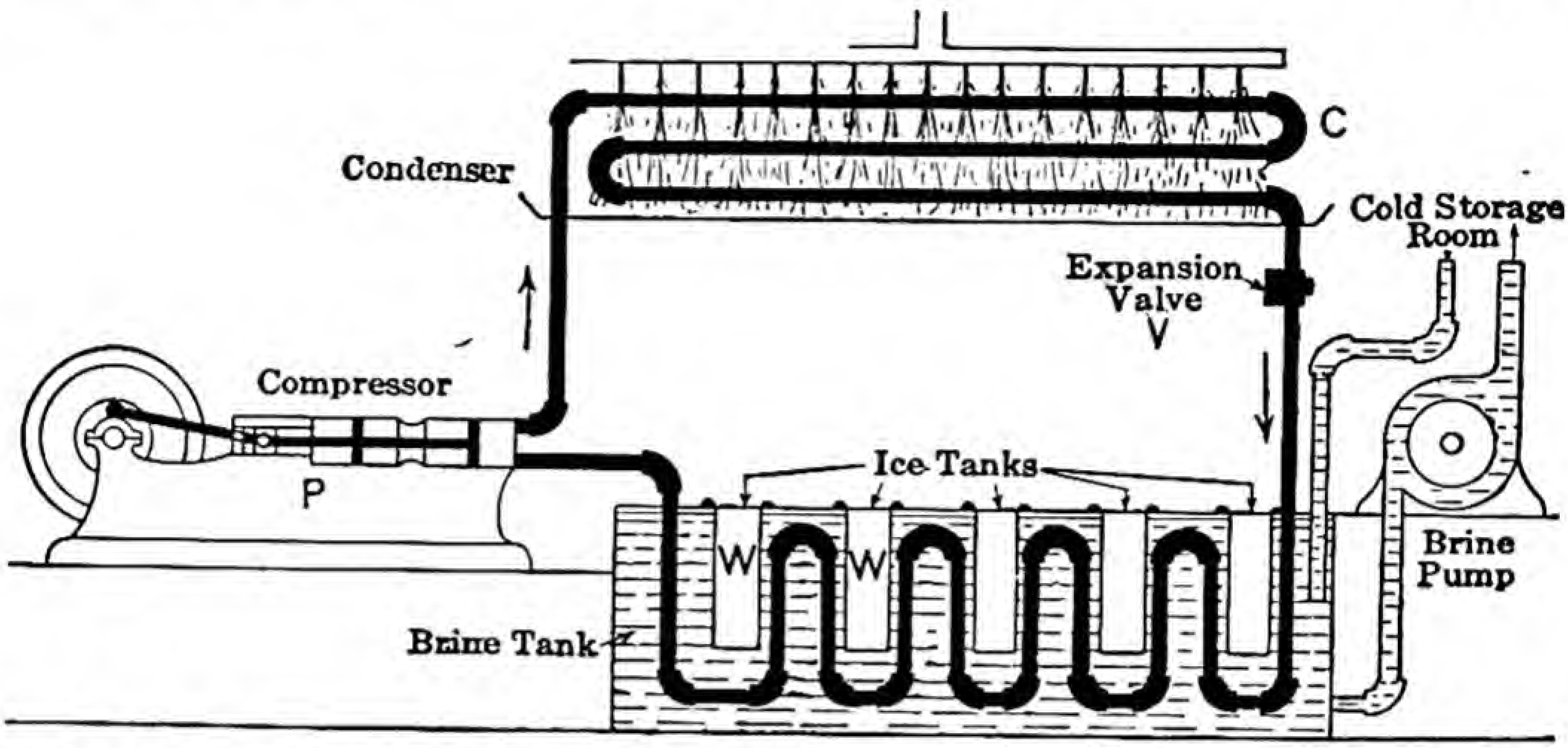


FIG. 67. Manufacture of ice. The compressed ammonia vapor is cooled by a spray of water at C, thus being recondensed to liquid. In expanding through the valve, V, the liquid is vaporized, heat disappearing.

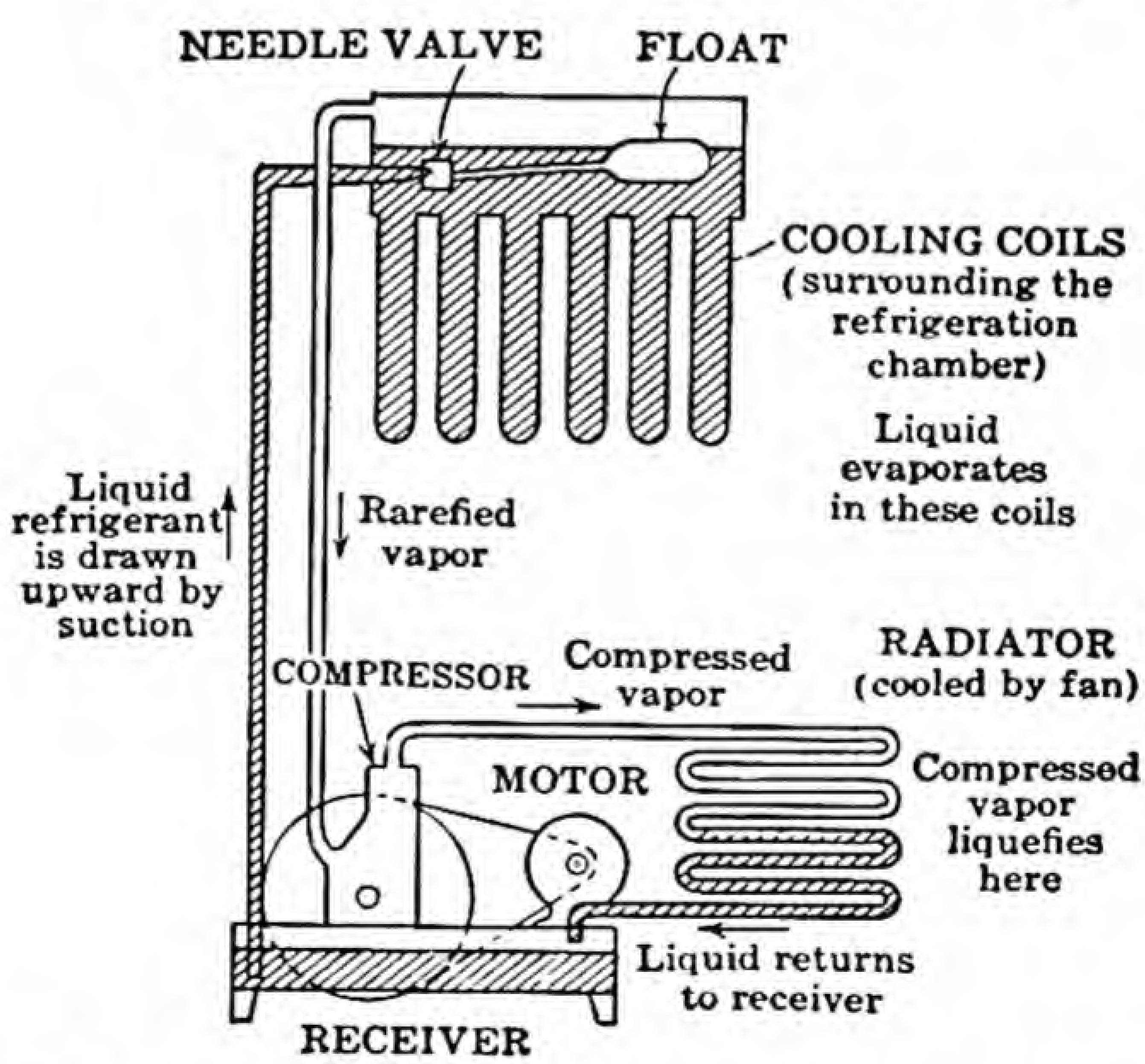


FIG. 68. Electrically driven household refrigerator.

melting of the solid and then the evaporation of the liquid. This is the basis of "Dry Ice" refrigeration.

Household refrigerators must employ some liquid that is non-toxic, non-corrosive, capable of being retained under low pressures, and with a reasonably high heat of vaporization. Fluorine-substituted hydrocarbons (§ 281) are the most widely used substances of this type.

In an electric refrigerator the vapor produced by the evaporation of the liquid is automatically recompressed by an electrically driven pump, then cooled by a stream of running water or by air, recondensed to a liquid, and restored to the system (Fig. 68). A *thermostat* insures that the motor shall operate only when the temperature rises above a certain point.

PROPERTIES OF REFRIGERANTS

	Heat of Evaporation at 0°C (cal/g)	Critical Temperature (°C)	Critical Pressure (atm)	Condenser Pressure (atm)	Evaporator Pressure (atm)	Relative Volume of Vapor Handled for Equal Refrigeration
Ammonia	301.6 *	132.4	111.5	11.5	2.33	3.8
Carbon dioxide	55.0	31.1	73.0	71.4	22.6	1.0
Sulfur dioxide	91.3	157.2	77.5	4.52	0.8	10.0
Methyl chloride	98.8	143.1	65.8	6.5	1.43	26.0

* Once more, observe a very high heat of evaporation, since ammonia, like water, is associated in the liquid state.

Refrigerators operated by a gas flame have the advantage of being noiseless. In one type ammonia gas is generated by heating a solution of the gas in water. The expelled gas is cooled by running water and collected in a condenser, under sufficient pressure to cause it to liquefy. The liquid ammonia, in vaporizing, absorbs heat. Finally the vapor is redissolved in water in an "absorber." The pressure is equalized in the different parts of the apparatus by the use of hydrogen in the low-pressure parts, to supplement the vapor pressure of ammonia. Some refrigerators use silica gel (§ 483), instead of water, as an absorbent.

► 157. Melting and Freezing

When we heat a crystalline substance to higher and higher temperatures the particles that compose it swing more and more violently about their mid-positions. Finally, at some definite temperature, the *melting point* of the crystal, they acquire sufficient energy to overcome the attractive forces between them, and the crystal collapses to a liquid.

Though a pure crystal, on being heated, melts at a definite temperature, the liquid so obtained may often be cooled below that temperature without resolidifying. Ice, for example, melts at 0°C. But water, if free from dust and air bubbles, may often be cooled several degrees below 0°C, without freezing, particularly if it is not stirred. A liquid that has been cooled below the melting point of the ordinary, stable solid form of that material is said to have been *supercooled.*

A supercooled liquid may be induced to crystallize by adding one or several small fragments of the expected crystalline material. Crystallization then begins at the corners and edges of the added solid material. *Heat is liberated in the freezing process;* hence, when freezing begins in a supercooled liquid, the temperature rises until it reaches the true freezing point of the material, then remains constant.

If we ask why inoculating a supercooled liquid with a crystal fragment will cause freezing to begin, the answer seems clear. The inoculation adds a fragment of the expected crystalline material, ready made, that is too massive and substantial to be broken down (as a flimsy crystalline nucleus might be) by chance collisions with surrounding liquid molecules. The added fragment is sure to contain billions of atoms or molecules, even though it is microscopic in size. Any molecule of the liquid approaching such an edge of such a particle is strongly attracted, and so perhaps bound fast. The freezing temperature is simply that at which deposition of new material along the edges of a comparatively *massive crystal particle* exactly balances the rate at which material becomes disengaged from the crystal.

► 158. Details of the Freezing Process

Figure 69 plots temperature against time, for a sample of water that is gradually cooled by being submerged in a *freezing mixture* (salt and ice). Notice the initial cooling (A to B) below 0°C (supercooling), followed by a rapid rise in temperature (B to C) as soon as freezing begins, on account of heat set free in the process of freezing. Thereafter, freezing continues (C to D) at a constant temperature (0°C for water). This constant temperature, maintained during the freezing of a liquid, is its *freezing point.* The freezing point, in Fig. 69, is represented by the horizontal part of the freezing-point curve, *not* by the lowest point of the curve, at which freezing begins.

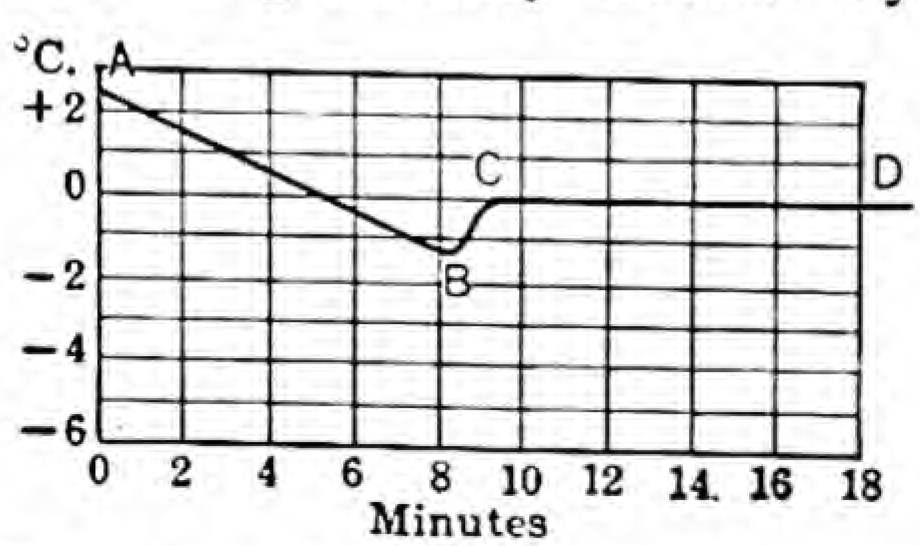


FIG. 69. Freezing-point curve for water.

The freezing point of a pure liquid is the same as the melting point of the crystals obtained in the freezing. This need be no mystery. The melting point or freezing point is simply the temperature at which melting of the solid and freezing of the resultant liquid proceed at the

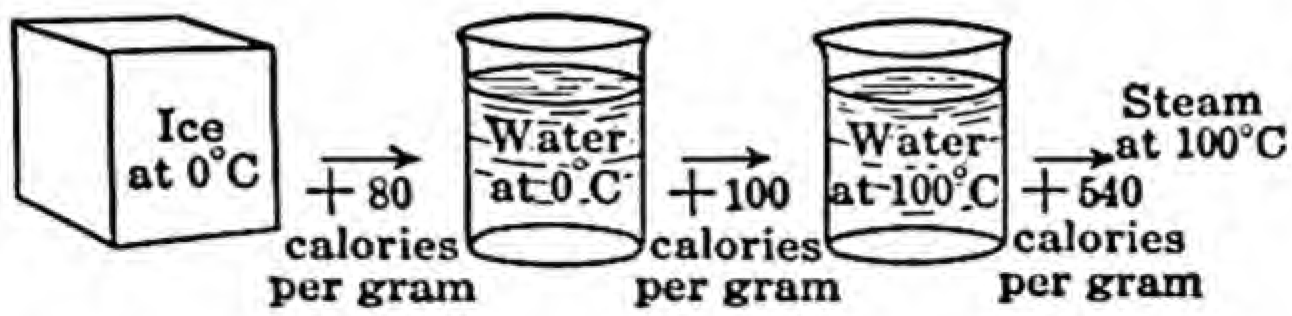


FIG. 70. Showing the successive quantities of heat needed to convert ice into steam.

same rate, when no heat is being yielded to or received from the surroundings; in consequence, solid and liquid may remain in contact indefinitely at the freezing or melting point, without any change in temperature. (Ex. 9.)

A definite quantity of heat is set free in *freezing* and disappears in *melting* a stated amount of any crystalline solid. This is because *a definite amount of energy must be expended in overcoming the attractive forces of the molecules for one another, in breaking down the crystal.* The heat that disappears in melting 1 gram of a crystalline substance is called its *heat of fusion* (about 79 calories for ice). When the liquid thus obtained resolidifies in crystalline form (*e.g.*, when water is frozen into ice), the same amount of heat is once more set free. (Ex. 10.)

159. Sublimation

Solids, like liquids, will vaporize at all temperatures, though the process is perceptible only with solids that happen to be particularly volatile. The passage of a substance from the solid state directly into the vapor state, and its recondensation as a solid, is termed *sublimation*. This process is often useful in purifying materials. For example, iodine is frequently purified by being submixed with a little potassium iodide, then sublimed. (The potassium iodide serves to remove bromine or chlorine, usually present in iodine as impurities.) In the lecture experiment shown in Fig. 71 crystals of iodine in the beaker gradually sublime, filling the beaker with purple vapors, which condense as beautiful purplish black spangles on the cold outer surface of a flask filled with water.

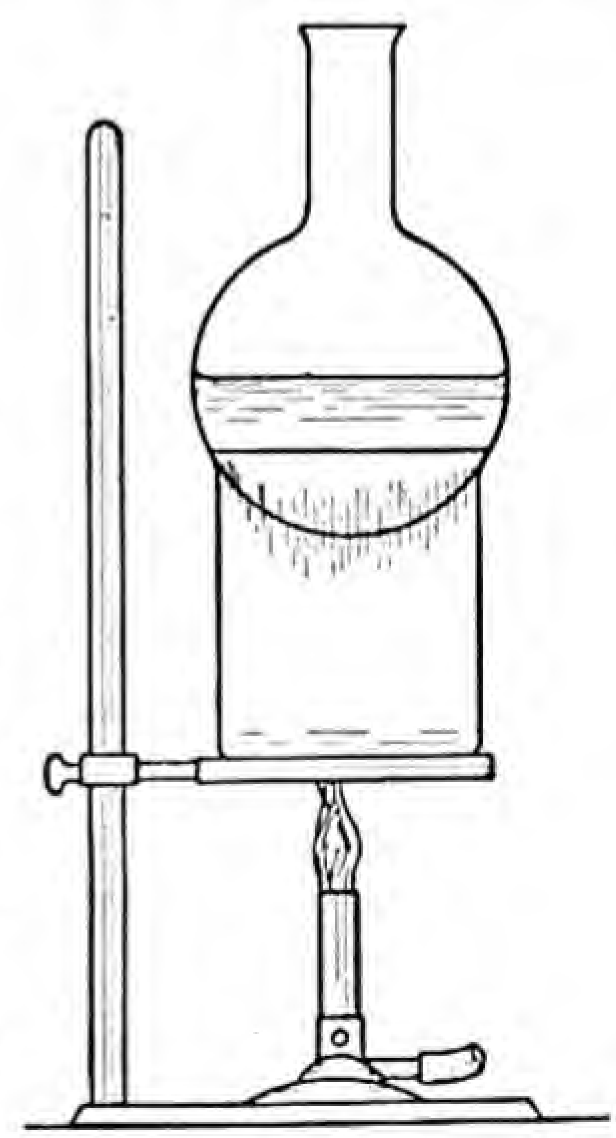


FIG. 71.

The heat that disappears (*i.e.*, the *energy* that is used) in vaporizing 1 gram of a solid is sometimes called its *heat of sublimation.* It is of course equal to the total heat that is needed, first to melt the solid, then to evaporate the resultant liquid.

160. Change of Crystal Form

When atoms, ions, or molecules fall into an orderly arrangement, in constructing a crystal, the particular arrangement chosen, hence the external form of the crystal, is usually determined by the *largest* of the several sorts of particles (§ 144). When several different arrangements are possible the most stable one is that in which the attractive forces within the crystal result in minimum potential energy (§ 67).

A material which can exist in several different crystalline forms is said to be *polymorphic* (*Greek:* many-formed). Polymorphic elements are said to be *allotropic* (*Greek:* other-turning).

At any chosen temperature, one of the crystalline forms of an element or compound is relatively *stable,* in that it will persist indefinitely without showing the least tendency to be transformed into the others. The other forms (of higher potential energy) are said to be *metastable.* Sometimes the metastable form or forms of a substance are rapidly converted into the stable form, especially when the substance is heated, or in the presence of a catalyst or solvent. In other instances, particularly at low temperatures, the metastable form (for example, the diamond form of carbon) may persist indefinitely, thus giving the impression of being stable.

If we alter the temperature we sometimes find that a different form of the substance becomes stable. Whenever this happens there is always some intermediate temperature at which both forms are stable and can remain indefinitely in contact with each other without either being converted into the other. This is an *equilibrium temperature,* often called a *transition* or *transformation temperature,* at which the two opposite transformations

$$\text{Form } A \rightleftharpoons \text{Form } B$$

proceed at equal rates. Turn to § 304 for an example.

Be sure not to miss the significance of such changes in crystal form. They are possible only because the ions or molecules that compose a crystal are not rigidly fixed in position, but swing back and forth over slight arcs. So a comparatively slight displacement of them from their original positions sometimes brings them into completely new ar-

rangements with respect to one another. The result is a completely different type of crystal.

161. The Phase Rule

In discussing changes of state we sometimes speak of molecules as passing from a liquid phase to a vapor phase, in evaporation; or from a solid phase to a vapor phase and back again, in sublimation; or from one solid phase into another, in changes of crystal form. The word *phase* evidently means ***any homogeneous portion of matter, whether continuous*** (as in a single crystal) ***or discontinuous*** (as in a handful of crystals or a spray of liquid droplets).

For example, if we had a solution of common salt, with some undissolved salt crystals beneath it, three phases would be present: the solid phase (discontinuous), the liquid or solution phase (continuous), and an overlying air and vapor phase (continuous). If two or more gases or vapors are placed in contact they will always intermingle to form a single homogeneous gaseous phase. In other words, no mixture can contain more than one gaseous phase; but it may contain several liquid phases (for example, separate layers of mercury, water, and oil), and any number of solid phases.

An important part of chemistry and physics is concerned with *phases in equilibrium* (a condition of balance between opposing forces or processes). For example:

1. Liquid and vapor phases are in equilibrium when they are in contact in a closed vessel (§ 151); the vapor then sets up a definite vapor pressure, which varies with the temperature.
2. Two different liquid phases (layered, the one over the other) are in equilibrium with each other and with a vapor phase at any temperature, over a wide range.
3. Liquid and solid phases, and a vapor phase (all of the same *substance*) are in equilibrium only at one temperature, the *freezing point* of the liquid (§ 158).
4. Two different solid phases (different forms of the same *substance*) are in equilibrium with each other, and with a vapor phase, only at one temperature, their *transformation* or *transition temperature* (§ 160).

Studies of such equilibria are complicated by the fact that the different phases, though individually *homogeneous*, are sometimes solutions, of variable composition. Moreover their *components* (namely, the independently variable substances that compose them) sometimes enter into chemical reactions with one another. (Ex. 11.)

If we now observe a given set of phases in equilibrium (for example, a solution in equilibrium with vapor and some undissolved solid) a very practical question is this: *If the observed phases are to be main-*

tained, in equilibrium with one another, must we rigidly adhere to some particular temperature and pressure and to some particular concentrations (of the components of a solution); *or can some of these conditions be somewhat altered, without causing any phase to disappear?* [1]

The answer to this question is always given by a simple rule called the *phase rule*, best presented in three parts:

1. The number of phases in any system in equilibrium is *at most* two greater than the number of components.

2. This maximum number of phases is possible only at a definite temperature, a definite pressure, and a definite concentration of each component in each phase.

3. When less than the maximum number of phases are present, then *for each phase that is missing* we may independently vary either temperature, pressure, or a concentration through at least a small range, without causing any phase to disappear. (Ex. 12.)

The number of conditions that may thus be varied is called the *variance*, [2] hence the phase rule may be expressed,

$$\underset{\text{Variance}}{V} = \underbrace{C + 2}_{\substack{\text{Maximum}\\ \text{possible}\\ \text{number of}\\ \text{phases}}} - \underset{\substack{\text{Actual}\\ \text{number of}\\ \text{phases}}}{P}$$

or, $P + V = C + 2$.

Applications are best illustrated by a table:

System	*C*	*P*	*V*	*Conclusion*
1. A pure liquid in equilibrium with its own vapor	1	2	1	You may vary the temperature without causing any phase to disappear.
2. Two different liquids, layered, in equilibrium with vapor	2	3	1	You may vary the temperature without causing any phase to disappear.
3. Solid, liquid, and vapor phases of a pure substance, in equilibrium	1	3	0	Temperature (the freezing point) is fixed and invariable.
4. Two different solid forms of same substance, in equilibrium with vapor	1	3	0	Temperature (the *transition point*) is fixed and invariable.

[1] In the four numbered examples above, for example, the temperature is found to be variable in the first two instances, but in the other two must be held constant if equilibrium is to be maintained.

[2] Formerly termed the *freedom*, which was an unsatisfactory term because it has another meaning in physical chemistry (§ 120).

5. A crystalline hydrate, in equilibrium with the crystalline anhydrous salt derived from it, a solution, and vapor	2	4	0	Temperature is fixed and invariable.
6. A solution containing two different dissolved substances in a liquid solvent, in equilibrium with vapor	3	2	3	You may vary the temperature, also the concentrations of both the dissolved substances, yet still have all the phases persist, in equilibrium.

(Ex. 13, 14.)

Technical Words

Saturated (as applied to the space above an evaporating liquid)—containing all the vapor that the space can *acquire* and *hold* at the given temperature, in contact with unevaporated liquid.

Standard atmospheric pressure or a pressure of **1 atmosphere**—the average pressure caused by the weight of the atmosphere, at sea level, in temperate latitudes. It is a pressure of 1033 grams per square centimeter or 14.7 pounds per square inch. It will elevate mercury in a barometer to a height of 760 mm, and is therefore often referred to as a pressure of 760 mm.

Vapor pressure, p. 173.

Boiling—rapid evaporation, accompanied by the formation of bubbles or vapor within the liquid. **Boiling point,** p. 174.

Vacuum evaporator or **vacuum pan,** p. 175.

Pressure cooker or **autoclave,** p. 175. **Critical temperature,** p. 176.

Critical pressure, p. 176.

Heat of vaporization, p. 177. **Heat of fusion,** p. 181.

Melting point or **freezing point**—the temperature at which the solid and liquid forms of any *pure* substance are in equilibrium (p. 183); in other words, the temperature at which they may remain indefinitely in contact with each other. For a somewhat impure material, melting point and freezing point are the somewhat unequal temperatures at which melting and freezing *begin* (in the absence of supercooling).

Supercooling—cooling a liquid below its freezing point, without the liquid being frozen.

Polymorphic, p. 182. **Allotropic,** p. 182.

Sublimation, p. 181. **Heat of sublimation,** p. 182.

Homogeneous—apparently uniform throughout, no portion of any sample being distinguishable in composition or properties from any other portion.

Phase—any *homogeneous* (but not necessarily continuous) portion of matter, *distinct in composition or properties from any other phases that may be present.* A handful of salt and sugar crystals, beneath a liquid solution, partly filling a bottle, would represent a system of four phases: two solid phases (salt and sugar), a liquid phase (the solution), and a gaseous phase (the mixture of air and water vapor that is in contact with the solution).

Variance, p. 184.

Component—one of the independently variable substances composing a mixture. (The term *independently variable* implies that no substance may be recognized as a component if it is derivable from other components by a chemical reaction.)

SUMMARY

► § 149. Names given to the chief processes involving changes of state.

► § 150. A description of some of the details of what happens in evaporation. Four means often taken for increasing the rate of evaporation. Explanation of each in terms of molecules.

► § 151. How we may demonstrate that the vapor escaping from an evaporating liquid sets up a pressure.

Name given to the pressure exerted by a vapor, when the space above the liquid has become saturated with vapor. What two factors determine how great this pressure shall be.

What variable is plotted along each axis, in a vapor-pressure curve.

► § 152. How we may determine whether a liquid is merely evaporating or is actually boiling.

How we may find the boiling point of a liquid at other than atmospheric pressure, from a table of vapor pressures or a vapor-pressure curve.

► § 153. What kinds of liquids are commonly evaporated in a vacuum evaporator and why. How spray drying is accomplished.

Another name given to a pressure cooker. What is accomplished by the use of a pressure cooker instead of an open boiler.

► § 154. A description of events when a liquid is heated within a closed vessel until the critical temperature is reached. Name given to the pressure that a liquid exerts at its critical temperature.

► § 155. Name given to the quantity of heat needed to vaporize a gram of any liquid. What becomes of the energy which thus disappears.

In what respect steam is a good carrier of heat and in what respect an inconvenient one.

► § 156. Several liquids commonly used in refrigeration.

A brief description of the operation of an electric refrigerator.

► § 157. Why a pure crystal melts at a definite temperature.

Conditions under which a liquid may be supercooled without freezing. How supercooling may be ended. What then happens to the temperature, and why.

► § 158. Sketch of a typical freezing curve. What variable is plotted along each axis. What represents the freezing point, on such a curve.

§ 159. Description of an experiment to illustrate sublimation. How one may calculate the heat of sublimation from other data.

§ 160. Name given to compounds that occur in several different crystalline forms. Corresponding name for elements.

Name given to a crystalline form that tends to be converted into a more stable form.

Name given to the temperature at which two different forms of a substance are in equilibrium with each other and with the vapor of the substance.

§ 161. Three technical words needed in the statement of the phase rule, and the definition of each. Statement of the rule, in three parts. The corresponding statement, as an algebraic equation.

Application to a typical case.

Exercises

1. Does water evaporate more rapidly into dry air than into moist air at the same temperature? Why?

2. Will clothing dry when hung out in weather so cold that water immediately freezes? Explain.

3. What sort of liquid must be used in the U-tube in Fig. 63? How will the displacement of the liquid in the U-tube vary with its density?

4. From Fig. 64 deduce the normal boiling point of each of the three liquids there indicated.

5. From Fig. 64 deduce the boiling points of the three liquids if the pressure over them is decreased to 50 cm, by means of an air pump.

6. From Fig. 64 determine the pressure under which water will boil at 30°C.

7. Explain why the surface tension of a liquid approaches zero as the critical temperature is approached.

8. The heat of evaporation of ammonia at refrigeration temperatures is roughly 310 calories per gram. Compare with the heat of fusion of ice (§ 158) to determine what weight of ammonia must be evaporated in a refrigerator, working with perfect efficiency, to freeze 1 gram of water. 255

9. What would a freezing curve look like if supercooling were prevented?

10. What quantity of heat is set free when one gram-formula weight of water freezes? 142

11. How many phases (including the vapor phase) are present in the freezing mixture in the outer jacket of an ice cream freezer? How many components?

12. Use the phase rule to determine whether the mixture mentioned in the preceding exercise finally reaches a definite and invariable temperature, if enough solid salt is used.

13. What is the variance of a system composed of two mutually soluble liquids (hence a single liquid phase), in equilibrium with vapor? What may therefore be varied, without altering the number of phases?

14. Use the phase rule to prove that it is impossible for three different solid phases to be in equilibrium with a liquid phase and a vapor phase, unless the system contains three or more components.

Chapter 13

PREPARATION OF ACIDS

VALENCE

► 162. Some Common Acids

The substances called *acids* may be recognized by three very simple tests:

1. The most active acids, in solution in water, taste *sour*. (One should, of course, make sure that they have been sufficiently diluted to be safe to taste.)

2. The most active acids turn blue litmus red.

3. All acids react with substances called *bases* (Example: NaOH) in such a manner that the properties of both acid and base disappear. Each is then said to have *neutralized* the other.

The first of these three characteristics of acids was doubtless the first to be observed. In fact, the word acid is related to the Latin *acer* and to a similar Sanscrit word, both meaning *sour*. But you will notice that the first two of the three tests apply only to the most active acids, whereas the third (ability to neutralize bases) is more general.

In the broadest sense, then, an *acid* is *any base-neutralizing substance*. In this sense, which was in vogue until about a century ago, the word acid includes a very wide range of substances, *containing no one element in common*. Sulfur dioxide, for example, may be termed an acid in the broadest sense of the word, since it reacts with and neutralizes sodium oxide (a base, in the most general sense):

$$\underset{\text{Sulfur dioxide}}{SO_2} + \underset{\text{Sodium oxide}}{Na_2O} \rightarrow \underset{\text{Sodium sulfite}}{Na_2SO_3}$$

This reaction takes place whether any solvent is present or not.

Nevertheless chemists, for about a century, have nearly always used the terms acid and base in a much narrower sense than that just indicated. They have been chiefly interested in reactions in water

as a solvent. The term *acid* is then conveniently limited to *base-neutralizing substances that contain hydrogen.* Many chemists have also limited the term *base* to *acid-neutralizing substances that contain the hydroxyl ion, OH^-.*

For beginners, it will seem less confusing if we refrain from passing, all at one bound, to the most general point of view. So this and the following chapter will be concerned only with *acids in the narrower sense,* that is to say, with *base-neutralizing substances containing hydrogen.* In a later chapter (§ 416) we shall examine the more general viewpoint, for those who wish to learn more about it.

Acids that contain no oxygen have names beginning with the prefix *hydro-.* Examples:

HF	HCl	HBr	HI	HCN	H_2S
Hydrofluoric acid (Hydrogen fluoride)	Hydrochloric acid (Hydrogen chloride)	Hydrobromic acid (Hydrogen bromide)	Hydriodic acid* (Hydrogen iodide)	Hydrocyanic acid (Hydrogen cyanide)	Hydrosulfuric acid (Hydrogen sulfide)

* Observe the spelling of this word, dropping the *o* in *hydro-*; also the pronunciation, *hy-drĭ-ŏd'-ic.*

The names in parentheses are preferred for these substances in *the gaseous state*, and the other names for *solutions.*

Acids that contain oxygen may differ in the number of atoms of oxygen in their formulas. Examples:

	$HClO$ Hypochlorous acid	$HBrO$ Hypobromous acid		
HNO_2 Nitrous acid	$HClO_2$ Chlorous acid	HIO_2 Iodous acid	H_2SO_3 Sulfurous acid	H_3PO_3 Phosphorous acid
HNO_3 Nitric acid	**$HClO_3$** Chloric acid	**HIO_3** Iodic acid	**H_2SO_4** Sulfuric acid	**H_3PO_4** Phosphoric acid
	$HClO_4$ Perchloric acid	HIO_4 Periodic acid		

Memorize the formulas of acids, here given in bold-faced type, that have names ending in "-ic." Then observe that each "*-ous*" acid contains 1 less oxygen atom, and each "*hypo—ous*" acid contains 2 less oxygen atoms than the corresponding "*-ic*" acid. On the contrary, each "*per—ic*" acid shown here contains 1 more oxygen atom than the corresponding "*-ic*" acid. (The prefix *per-* is often used with a somewhat different meaning.)

▶ 163. Naming Salts

When an acid reacts with a metal, metallic oxide, or metallic hydroxide, one of the products is a *salt.* Let us compare the names and conventional formulas of a few salts with those of the corresponding acids:

HCl Hydrochloric acid	$NaCl$ Sodium chloride	$MgCl_2$ Magnesium chloride	$AlCl_3$ * Aluminum chloride
$HClO$ Hypochlorous acid	$NaClO$ Sodium hypochlorite	$Mg(ClO)_2$ Magnesium hypochlorite	$Al(ClO)_3$ Aluminum hypochlorite
H_2SO_4 Sulfuric acid	Na_2SO_4 Sodium sulfate	$MgSO_4$ Magnesium sulfate	$Al_2(SO_4)_3$ Aluminum sulfate
H_2SO_3 Sulfurous acid	Na_2SO_3 Sodium sulfite	$MgSO_3$ Magnesium sulfite	$Al_2(SO_3)_3$ Aluminum sulfite

* This formula is used for simplicity; the true formula is Al_2Cl_6.

Observe that salts derived from the "*hydro—ic*" acids drop the prefix *hydro-* of the acid, and take the ending *-ide;* salts derived from "*-ic*" acids take the ending *-ate;* salts derived from "*-ous*" acids take the ending *-ite.* If an acid has the prefix *hypo-* or *per-*, this is retained in the names of salts derived from the acid. (Ex. 1–4.)

▶ 164. Preparation of Acids from Non-metallic Oxides

Acids containing oxygen may very often be prepared by direct union of non-metallic oxides with water. Important examples:

$$\underset{\text{Sulfur trioxide}}{SO_3} + H_2O \rightarrow \underset{\text{Sulfuric acid}}{H_2SO_4}$$

$$\underset{\text{Nitrogen pentoxide}}{N_2O_5} + H_2O \rightarrow \underset{\text{Nitric acid}}{2HNO_3}$$

$$\underset{\text{Phosphorus pentoxide}}{P_2O_5} + 3H_2O \rightarrow \underset{\text{Phosphoric acid}}{2H_3PO_4}\ *$$

* The water needs to be heated; otherwise the first product is *metaphosphoric* acid, HPO_3, which then gradually combines with more water to form ordinary phosphoric acid, often called *orthophosphoric* acid, H_3PO_4.

Sometimes the reaction is reversible. Important examples:

$$\underset{\text{Carbon dioxide}}{CO_2} + H_2O \rightleftharpoons \underset{\text{Carbonic acid}}{H_2CO_3}$$

$$\underset{\text{Sulfur dioxide}}{SO_2} + H_2O \rightleftharpoons \underset{\text{Sulfurous acid}}{H_2SO_3}$$

Note again the use of the double arrow, $\rightleftharpoons$, to represent a reversible reaction. No matter how long we leave carbon dioxide or sulfur dioxide in contact with water these gases can never be completely transformed into acid. The obvious reason is that *the forward reaction, in which the oxide combines with water to form the acid, soon comes to proceed at the same rate as the reverse reaction, in which the acid is decomposed.* We have here another example of chemical equilibrium. *Neither of the oppositely directed reactions in a chemical equilibrium can ever become complete, no matter how long the materials are left in contact.* (Ex. 5–8.)

The acids and non-metallic oxides concerned in the five preceding formulations are important substances, whose formulas should be memorized.

► 165. Preparation of Volatile Acids

Volatile acids (those that are gaseous or readily vaporized) are conveniently prepared *by treating their salts with a slightly volatile acid* (usually sulfuric or phosphoric acid). Here are three examples:

1. In preparing *acetic acid*, on a small scale in the laboratory, a dry acetate is placed in a flask (*F*, Fig. 72), and concentrated sulfuric acid

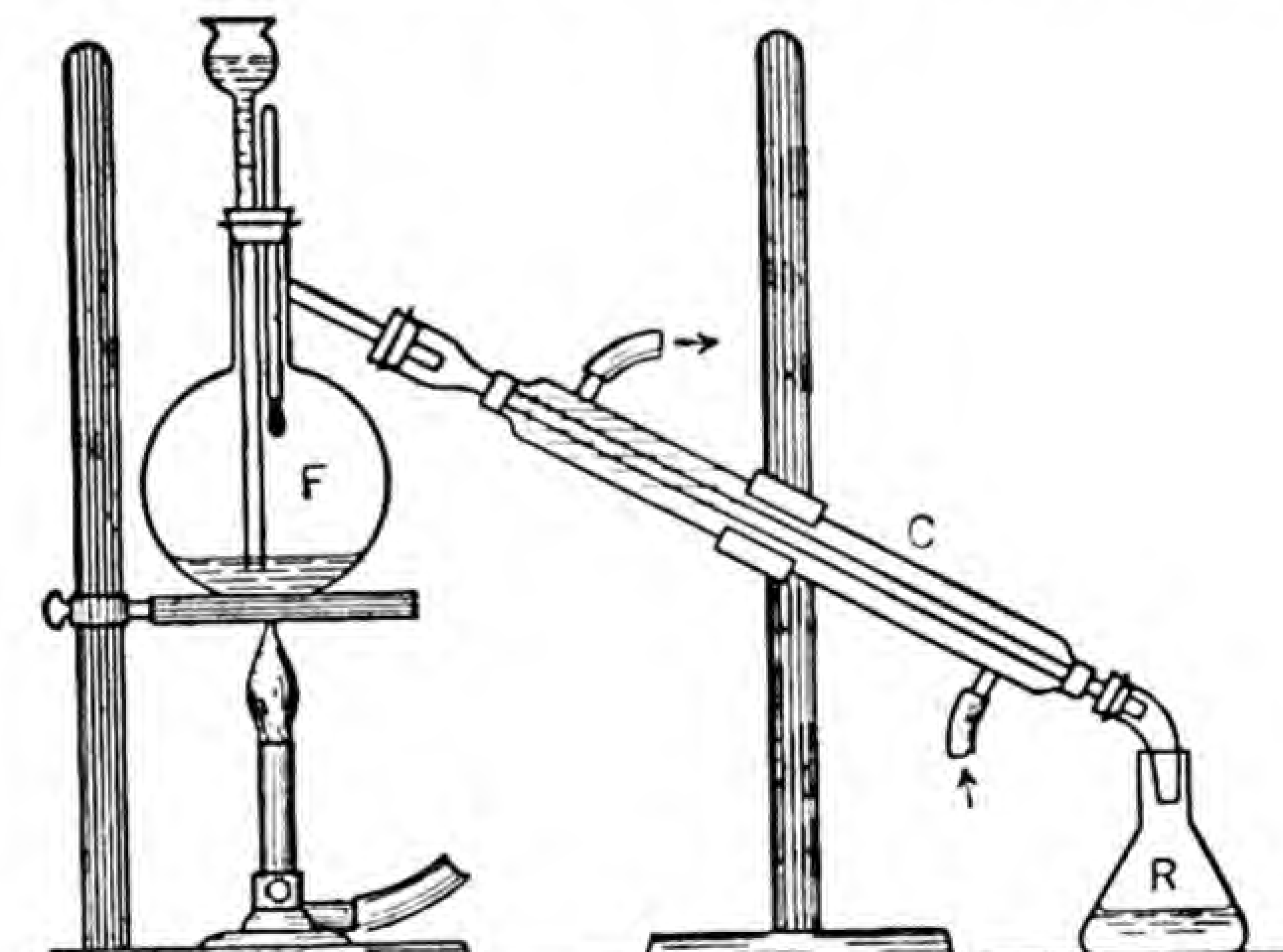


FIG. 72. Preparation of acetic acid as a lecture demonstration.

is slowly added through a thistle tube while the mixture is gently heated. The volatile acid, thus set free, passes into a condenser, *C*, cooled by running water. Here it condenses to a liquid, which collects in the receiver, *R*:

$$\underset{\text{Sodium acetate}}{NaC_2H_3O_2} + \underset{\text{Sulfuric acid}}{H_2SO_4} \rightarrow \underset{\text{Sodium hydrogen sulfate}}{NaHSO_4} + \underset{\text{Acetic acid}}{HC_2H_3O_2}\uparrow$$

Observe the use of an arrow, pointing upward, to direct attention to the fact that some product of a reaction is volatile and escapes as a gas or vapor. (Ex. 9.)

2. In preparing *nitric acid* in the laboratory, we use a glass-stoppered retort (Fig. 73), rather than a flask, since strong nitric acid attacks cork and rubber.

$$\underset{\text{Sodium nitrate}}{NaNO_3} + H_2SO_4 \rightarrow \underset{\text{Sodium hydrogen sulfate}}{NaHSO_4} + \underset{\text{Nitric acid}}{HNO_3} \uparrow$$

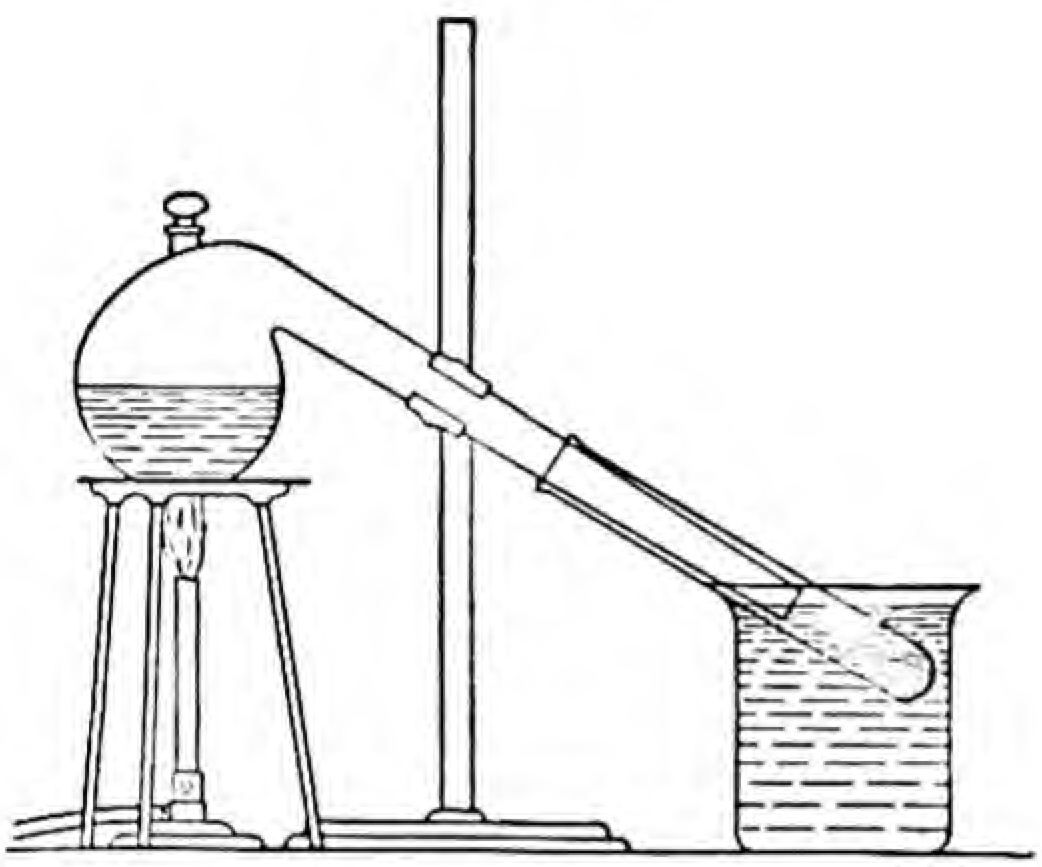


FIG. 73. Preparation of nitric acid as a lecture demonstration.

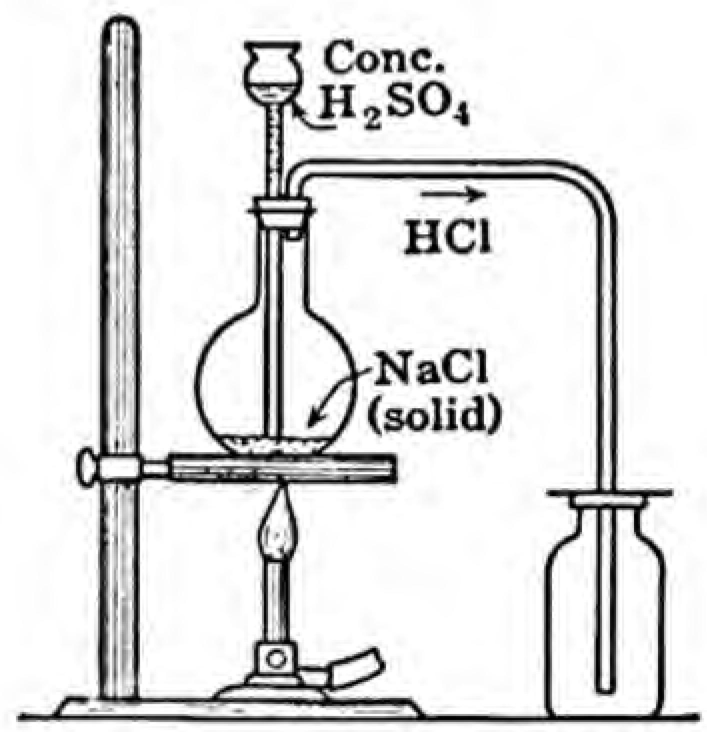


FIG. 74. Preparation of hydrogen chloride as a lecture demonstration.

3. If we treat sodium chloride, NaCl (common salt), with sulfuric acid the product is a colorless gas, *hydrogen chloride*, HCl (Fig. 74):

$$\underset{\text{Sodium chloride}}{NaCl} + H_2SO_4 \rightarrow NaHSO_4 + \underset{\text{Hydrogen chloride (gas)}}{HCl} \uparrow$$

When the hydrogen chloride gas is dissolved in water a chemical reaction takes place, forming the solution that we call *hydrochloric acid* (more about this in § 186). (Ex. 10.)

Instead of the sodium salts of the three acids just considered we might have used salts of some other metal, for example, magnesium salts. The procedure would have been the same, but the balanced equations would look somewhat different:

$$\underset{\text{Magnesium nitrate}}{Mg(NO_3)_2} + H_2SO_4 \rightarrow \underset{\text{Magnesium sulfate}}{MgSO_4} + 2HNO_3 \uparrow$$

$$\underset{\text{Magnesium acetate}}{Mg(C_2H_3O_2)_2} + H_2SO_4 \rightarrow MgSO_4 + 2HC_2H_3O_2 \uparrow$$

$$\underset{\text{Magnesium chloride}}{MgCl_2} + H_2SO_4 \rightarrow MgSO_4 + 2HCl \uparrow$$

► 166. Radicals

The preceding equations show that certain atoms have a very decided tendency to form *groups of atoms*, often called *radicals*, which remain together in spite of chemical transformations that involve the rest of the material. Thus the nitrate radical (NO_3) and the acetate radical ($C_2H_3O_2$) remain intact in chemical transformations that transform sodium or magnesium salts containing these radicals into nitric or acetic acid.

Radicals of *organic compounds* (compounds of carbon) are not separately examinable substances. They are merely *groups of atoms*—parts of molecules—which act as a unit in chemical reactions, in as intimate and enduring an association as any Three Musketeers. Inorganic (non-carbon) radicals are usually electrically charged particles (ions), which behave as nearly independent molecules. Examples:

NH_4^+	OH^-	NO_3^-	$C_2H_3O_2^-$	SO_4^{--}	PO_4^{---}
Ammonium-ion	Hydroxyl-ion	Nitrate ion	Acetate ion	Sulfate ion	Phosphate ion

Observe differences in charge. (Ex. 11.)

► 167. Valence

Let us list and compare some formulas that have appeared in the last few pages, or that we shall presently need to use:

Hydrogen Compounds	*Sodium Compounds*	*Magnesium Compounds*	*Aluminum Compounds*
HCl Hydrochloric acid	$NaCl$ Sodium chloride	$MgCl_2$ Magnesium chloride	$AlCl_3$ Aluminum chloride
HOH Water	$NaOH$ Sodium hydroxide	$Mg(OH)_2$ Magnesium hydroxide	$Al(OH)_3$ Aluminum hydroxide
$HC_2H_3O_2$ Acetic acid	$NaC_2H_3O_2$ Sodium acetate	$Mg(C_2H_3O_2)_2$ Magnesium acetate	
HNO_3 Nitric acid	$NaNO_3$ Sodium nitrate	$Mg(NO_3)_2$ Magnesium nitrate	
H_2CO_3 Carbonic acid	Na_2CO_3 Sodium carbonate	$MgCO_3$ Magnesium carbonate	
H_2SO_3 Sulfurous acid	Na_2SO_3 Sodium sulfite	$MgSO_3$ Magnesium sulfite	
H_2SO_4 Sulfuric acid	Na_2SO_4 Sodium sulfate	$MgSO_4$ Magnesium sulfate	
H_3PO_4 Phosphoric acid	Na_3PO_4 Sodium phosphate	$Mg_3(PO_4)_2$ Magnesium phosphate	

This table makes it easy to understand what is meant by *valence* Most simply expressed, valence is a number that tells how many atoms of hydrogen a given atom or radical appears to *combine with*, in forming an acid, or will *replace*, in converting the acid into a salt.

For example, our table shows that Cl, and the radicals (ions) (OH), (NO_3), and ($C_2H_3O_2$), are all alike in *combining with* one atom of hydrogen, to form HCl, HOH, HNO_3, $HC_2H_3O_2$. They are therefore said to be *univalent* or to have a valence of 1. But the radicals (CO_3), (SO_3), and (SO_4) each combine with two atoms of hydrogen to form H_2CO_3, H_2SO_3, H_2SO_4. They are therefore said to be *bivalent*, or to have a valence of 2. Similarly the radical (PO_4), in forming H_3PO_4, is *tervalent*, namely, has a valence of 3.

Next we observe that all the sodium compounds appear to be derived from the hydrogen compounds by *replacing* one or more hydrogen atoms, in the conventional formulas of these compounds, by an *equal number* of atoms of sodium. So, if hydrogen is given a valence of 1, that of sodium must also be 1. Comparing the third column of the table with the two preceding ones, we see that each atom of magnesium replaces two hydrogen atoms (in 2HCl or H_2SO_4, for example) in forming $MgCl_2$ or $MgSO_4$. Magnesium therefore has a valence of 2. Similarly, aluminum has a valence of 3. (Ex. 12.)

► 168. Ionic Valence

The idea of valence came into chemical thinking about 1852, in the manner in which we have obtained it, namely, as a result of a comparison of formulas. When ions came to be recognized, it was observed that *the valence of an ion is a measure of its electrical charge*. For example, all the sodium and magnesium salts in the table on the preceding page form ionic crystals (§ 142), in which the sodium and magnesium exist as positively charged ions. Let us represent the sodium ion by Na^+. The formula of sodium sulfate (deduced as in § 40) is Na_2SO_4; in other words, there are two sodium ions ($2Na^+$) in the crystal, and thus two positive charges, for every sulfate ion. The sulfate ion must therefore carry a double negative charge, hence the formula SO_4^{--}, *since the crystal as a whole is electrically neutral*. In the same way we see that the phosphate ion, in Na_3PO_4, must carry a triple negative charge, to offset the triple positive charge of three Na^+ ions; hence the formula of the phosphate ion must be PO_4^{---}.

Turning next to magnesium sulfate, $MgSO_4$, we see that, if sulfate ion is written SO_4^{--}, then magnesium ion must be Mg^{++}, to make the

crystal as a whole electrically neutral. Similarly for other ions. We discover that *the charge for every ion is that indicated by its valence.*

Valence that indicates the charge on an ion is called *ionic valence.* It is positive for cations (including metallic ions and ammonium ion, NH_4^+) and negative for anions (including non-metallic ions). (Ex. 13.)

► 169. Valences of Some Common Ions

Here are the valences of a few of the most common ions:

CATIONS

Valence +1: Na^+ K^+ NH_4^+ Ag^+

Valence +2: Mg^{++} Ca^{++} Sr^{++} Ba^{++} Sn^{++} (In any *stannous* salt) Cu^{++} (In any *cupric* salt) Fe^{++} (In any *ferrous* salt)

Mn^{++} (In any *manganous* salt) Pb^{++} (In most *lead* salts) Hg_2^{++} (In any *mercurous* salt) Hg^{++} (In any *mercuric* salt)

Valence +3 *: Al^{+++} Cr^{+++} (In any *chromic* salt) Fe^{+++} (In any *ferric* salt)

Valence +4 *: Sn^{++++} (In any *stannic* salt)

* Actually, compounds of these and other elements displaying a valence of +3 or more almost always exist in the covalent rather than in the ionic condition (§ 244).

The cations for which no names are given have been named in previous pages. With rare exceptions, they represent the only valence of the given element. If a name is given there is another valence of less importance. The two valences of iron and mercury are of equal importance. Observe the presence of two mercury atoms in mercurous ion.

The endings -ous and -ic for cations represent the *lower* and *higher,* respectively, of two common valences.

ANIONS

Valence −1: Cl^- (In any *chloride*) Br^- (In any *bromide*) I^- (In any *iodide*) OH^- (In any *hydroxide*) ClO^- (In any *hypochlorite*) ClO_3^- (In any *chlorate*)

ClO_4^- (In any *perchlorate*) NO_2^- (In any *nitrite*) NO_3^- (In any *nitrate*) CN^- (In any *cyanide*) $C_2H_3O_2^-$ (In any *acetate*) CNS^- (In any *thiocyanate*) MnO_4^- (In any *permanganate*)

Valence -2:	O^{--} In any *oxide*	S^{--} In any *sulfide*	SO_3^{--} In any *sulfite*	SO_4^{--} In any *sulfate*	
	$S_2O_3^{--}$ In any *thiosulfate*	CO_3^{--} In any *carbonate*	$C_2O_4^{--}$ In any *oxalate*	CrO_4^{--} In any *chromate*	$Cr_2O_7^{--}$ In any *dichromate*
Valence -3:	PO_4^{---} In any *phosphate*	$Fe(CN)_6^{---}$ In any *ferricyanide*			
Valence -4:	$Fe(CN)_6^{----}$ In any *ferrocyanide*				

Observe the names of five different anions containing sulfur, and seven containing carbon.

If the student will learn the names and formulas of the cations and anions here given he will have no difficulty in writing the formulas for most of the inorganic compounds to be encountered in this course. The clue to the formula is always in the fact that *the ions must be taken in proper proportions to make an electrically neutral crystal or solution.* Thus ferrous acetate must have two acetate ions (valence of each, -1) for every ferrous ion (valence $+2$); hence the formula $Fe(C_2H_3O_2)_2$. Similarly, ferric sulfate is $Fe_2(SO_4)_3$, and silver sulfide is Ag_2S. These are all merely *conventional formulas*, representing *relative numbers of ions*. For this reason use the simplest formula that will serve. Thus write $ZnSO_4$, not $Zn_2(SO_4)_2$.

What is needed now is a little practice in writing formulas. (Ex. 14–21.)

► 170. Non-Ionic Valence

Many substances, whether in gaseous, liquid, or solid condition, exist as electrically neutral molecules, rather than as ions. Examples are CO_2, H_2O, NH_3, CH_4. The atoms within such electrically neutral molecules are said to have *non-ionic valence*, often called *covalence*. It may be given a numerical value, but is neither positive nor negative.

In an ion containing two or more atoms (the acetate ion, $C_2H_3O_2^-$, for example), the ion as a whole possesses ionic valence, but the atoms within the ion are linked with one another in the same manner as within neutral molecules and hence possess non-ionic valence. Discussion of non-ionic valence will be postponed to a later chapter, since we shall then be better prepared to understand its cause and nature.

▶ 171. Valence Number

The valence number of an element is *apparent valence*, calculated by an arbitrary rule:

1. Consider each hydrogen atom as having a unit positive charge (except in metallic hydrides, in which its charge is -1).

2. Consider each oxygen atom as having a double negative charge (except in peroxides, in which its charge is assumed to be -1).

3. See what the charge on any other atom needs to be in order to account for the total charge on any specified molecule or ion.

For example, in sulfuric acid, H_2SO_4, the two hydrogen atoms together would possess a charge of $+2$; the four oxygen atoms together would possess a charge of -8; the sulfur atom therefore must possess a charge of $+6$ in order to make the whole molecule electrically neutral. Then $+6$ is the valence number of sulfur in sulfuric acid.

Next consider the nitrate ion, NO_3^-. Here the three oxygen atoms together possess a charge of -6; the nitrogen atom must therefore possess a charge of $+5$, in order that the ion as a whole may have a charge of -1, as indicated by its formula. Then $+5$ is the valence number of nitrogen in nitrate ion. The reader should pause to show that the valence number of each carbon atom in oxalic acid, $H_2C_2O_4$, is $+3$; and that of manganese in the permanganate ion, MnO_4^-, is $+7$.

Let us emphasize again that valence number is *apparent valence*, obtained by an *arbitrary rule* that does not always square with what is known about the manner of combination of the atoms. For example, the hydrogen and oxygen, in the examples just given, are really united with the other atoms by non-ionic valence, neither positive nor negative; and carbon, in oxalic acid, really has a non-ionic valence (covalence) of four.

For monatomic ions, such as Na^+ and Cl^-, the ionic valence is the same as the valence number. But non-ionic valence, within a molecule or within a complicated ion, need not agree with the valence number, which is calculated in an arbitrary way, ignoring some principles we shall encounter in a later chapter. (Ex. 22–24.)

▶ 172. Relative Weights of Reacting Substances

In an earlier chapter (§ 49) we had a little experience in calculating what weight of one substance corresponds to a definite weight of another, in a balanced chemical equation. There are actually two different methods for solving such problems:

1. *When the weight mentioned in the problem is easily seen to be a simple fraction or simple multiple of the weight of that substance indicated by the balanced chemical equation.*

Required, for example, what weight of sodium carbonate is needed to produce 1 gram of carbon dioxide, in the reaction:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2\uparrow$$

Indicated: 1 gram-formula weight = 106 grams; 2 gram-formula weights = 2 × 58.5 = 117 grams; 1 mole = 44 grams

Reason thus: The weight of carbon dioxide mentioned happens to be an even $\frac{1}{44}$ of the indicated weight of that substance. So we shall need $\frac{1}{44}$ of the indicated weight of sodium carbonate, namely, $\frac{1}{44} \times 106 = 2.41$ grams.

2. *When the weight mentioned in the problem seems not to be simply related to the weight of that substance indicated by the equation.*

Required, for example, what weight of carbon dioxide can be produced from 500 grams of sodium carbonate.

Refer to the preceding equation and reason thus: The 500 grams mentioned is not simply related to the indicated weight of sodium carbonate (106 grams). But the equation shows that the weight of carbon dioxide obtained is always *less* than the weight of the sodium carbonate that produced it; more precisely, the carbon dioxide weighs $\frac{44}{106}$ as much as the sodium carbonate that produced it. So 500 grams of sodium carbonate will produce $\frac{44}{106} \times 500 = 207$ grams of carbon dioxide.

We see that the answer to this problem was obtained by multiplying the *given weight* (of Na_2CO_3) by the ratio of indicated weights, $\frac{CO_2}{Na_2CO_3} = \frac{44}{106} = 0.414$. Such a ratio of weights, indicated by a chemical equation, is called a *chemical factor* or sometimes a *gravimetric* (weight-measuring) *factor*. Then, in multiplying,

$$Na_2CO_3 \text{ (given weight)} \times \frac{CO_2}{Na_2CO_3} \text{ (chemical factor)}$$

treating the chemical symbols as if they were algebraical symbols, Na_2CO_3 cancels out and the result is a weight of CO_2.

On the basis of the same chemical equation, we may calculate another chemical factor and use it in another problem:

$$\frac{2NaCl}{Na_2CO_3} = \frac{117}{106} = 1.104$$

When any stated weight of Na_2CO_3 (say 500 grams) is multiplied by this factor, Na_2CO_3 will obviously cancel out and the result will be a weight of NaCl.

The substance whose weight is *required* must obviously always appear in the numerator of the factor (above the line), and the one whose weight is *given* must appear in the denominator (below the line). One great advantage of the use of chemical factors is that they may often be found, already calculated, in tables in chemical handbooks. (The instructor may exhibit such a table.)

The student should learn both the preceding methods and be quick to judge which to use in any given problem. The first method is the better for making quick estimates, even when the weight mentioned in the problem is *not quite* a simple multiple or simple fraction of the weight of that substance that is indicated in the chemical equation.

The second method is preferred by chemists whenever a chemical factor, calculated in advance or looked up in a table, can be used in a number of different problems, *all of the same sort.* This frequently happens in analytical laboratories, where one may need, for example, to determine the percentage of sulfur in dozens or hundreds of different samples of a food stuff or an industrial product, by separating and weighing the sulfur as barium sulfate. The various weights of barium sulfate actually obtained need only to be multiplied by the factor $S/BaSO_4 = 0.13735$ to obtain the corresponding weights of sulfur in the original samples. (Ex. 25–33.)

Do not use proportion, cross-multiplication, or any other thought-evading devices in such problems. Our purpose is not to obtain numerical answers but to learn to reason.

Technical Words

Salt, p. 190. **Acid,** p. 189. **Radical,** p. 193. **Valence,** p. 194. **Univalent, bivalent, tervalent,** p. 194. **Ionic valence,** p. 195. **Non-ionic valence** or **covalence,** p. 196. **Valence number,** p. 197. **Chemical factor,** p. 198. **Organic compound,** p. 193. **Cation, anion,** p. 159.

Summary

§ 162. What properties enable us to recognize an acid.

A broad and a narrow definition of the word *acid*.

Names of a few common acids.

► § 163. How the prefix and suffix of the name of an acid suggest the name of any salt derived from the acid.

► § 164. A method for preparing acids from non-metallic oxides. Two such reactions that become complete and two that remain incomplete.

Why neither of the oppositely directed reactions in a chemical equilibrium can ever become complete.

► § 165. A name given to acids that are gaseous or readily vaporized.

Sketch of apparatus and a brief description to indicate how acetic acid and nitric acid, respectively, are prepared. Equations to represent these reactions.

Preparation of hydrogen chloride, with an equation. How hydrogen chloride may be converted into hydrochloric acid.

► § 166. A name given to a group of atoms that remain together in spite of chemical transformations. Which of such groups are really independent ions and which are merely parts of molecules. Name given to substances containing the hydroxyl radical or ion.

► § 167. What we mean by valence.

► § 168. What we mean by ionic valence.

► § 169 Meanings of the endings -ous and -ic, for cations. How we may determine the formu a of a salt composed of ions of known formulas.

► § 170. Examples of compounds in which we have non-ionic valence.

► § 171. What we mean by valence number. An illustration of how the valence number of sulfur in H_2SO_4 or of nitrogen in NO_3^- may be determined. When ionic valence is the same as valence number.

► § 172. The standard form for arranging an equation for a chemical reaction, with the actual and indicated weights.

Two methods for solving problems dealing with relative weights.

What we mean by chemical factors. An example.

Exercises

1. By analogy with the formulas of the chlorides, write names and formulas of the sodium, zinc, and aluminum salts derived from hydrofluoric and hydrobromic acids.

2. What name is given to salts derived from nitrous acid? Write formulas for three examples.

3. Write names and formulas for three salts derived from periodic acid.

4. Name the acids from which the following salts are derived: sodium metaborate, $NaBO_2$; sodium sulfide, Na_2S; magnesium cyanide, $Mg(CN)_2$; ammonium hypobromite, NH_4BrO.

5. How many moles of sulfur dioxide combine with water for each mole of sulfurous acid produced? What volume will this sulfur dioxide occupy under standard conditions, and what will it weigh?

6. How many gram atoms and what actual weight of oxygen combine with each gram atom of phosphorus in forming phosphorus pentoxide? 250, 400

7. How many moles and what actual weight of nitric acid can be produced from one mole of nitrogen pentoxide? 200, 126

8. Write and balance equations to indicate that chlorine monoxide, Cl_2O, combines reversibly with water to produce hypochlorous acid.

9. What weight of sodium acetate is needed to produce $\frac{1}{10}$ mole of acetic acid? 820

10. How many moles and what actual weight of sodium chloride would you need to prepare 2.24 liters of hydrogen chloride gas, under standard conditions? 100, 585

11. What meaning would you give the term gram radical? Illustrate for the nitrate radical.

12. Complete the last column in the table on p. 193.

13. From the formula of ammonium phosphate, $(NH_4)_3PO_4$, and the fact that the phosphate ion bears a triple negative charge, derive the formula of the ammonium ion. From this and the formula of ammonium sulfite, $(NH_4)_2SO_3$, derive the formula of the sulfite ion.

14. Write formulas for magnesium bromide, ammonium sulfide, potassium sulfite, calcium sulfate, and zinc acetate.

15. Write formulas for zinc iodide, silver sulfite, potassium carbonate, lead nitrate, ferric sulfide.

16. From the formula of mercuric acetate, $Hg(C_2H_3O_2)_2$, in comparison with that of acetic acid, explain how one would find the valence of mercury in mercuric compounds.

17. Oxalic acid is $H_2C_2O_4$. From this deduce the valence of the anion in this acid. Write formulas for ammonium oxalate, ferrous oxalate, ferric oxalate, and aluminum oxalate.

18. Write formulas for sodium chromate, potassium dichromate, cupric nitrate, manganous chloride, magnesium chlorate, ammonium ferrocyanide, and potassium ferricyanide.

19. Potassium permanganate is $KMnO_4$. What is the valence of the permanganate ion? Write formulas for calcium permanganate, permanganic acid, manganous hydroxide, ferric oxide, and ferrous phosphate.

20. Write formulas and charges of the anions in Exercise 12.

21. Write names and formulas for the ammonium, ferrous, and ferric salts of hydrofluoric, hydrobromic, hydriodic, and hydrocyanic acid.

22. Show that arsenic in the arsenate ion, AsO_4^{---}, has the same valence number as in arsenic pentoxide As_2O_5.

23. Show that the nitrogen in ammonia gas, NH_3, has the same valence number as in the ammonium ion, NH_4^+.

24. Find the valence number of sulfur in sulfur dioxide gas, sulfite ion, sulfide ion, sulfate ion, and the thiosulfate ion, $S_2O_3^{--}$.

In the following problems use exact atomic weights and logarithms, and show results to 4 figures.

25. Find the numerical value of the chemical factor for P_2O_5 in $Ca_3(PO_4)_2$. 458

26. Show how to use the chemical factor $Cl/AgCl = 0.2474$ in finding the weight of chlorine corresponding to any specified weight of silver chloride.

27. In the reaction

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$$

find a chemical factor for calculating the weight of sodium chloride corresponding to any observed weight of silver chloride. 408

28. Find the numerical value of a chemical factor that will permit one to calculate the weight of potassium oxide, K_2O, corresponding to any observed weight of potassium chloroplatinate K_2PtCl_6. 194

29. What weight of boric oxide, B_2O_3, corresponds to each gram of boric acid, H_3BO_3? (Observe that two molecules of the acid are required to furnish the boron in the formula of boric oxide.) 563

30. Find a chemical factor to be used in finding the weight of nitrogen corresponding to any given weight of ammonium sulfate, $(NH_4)_2SO_4$. 212

31. From the chemical factor $CO_2/CaCO_3 = 0.440$, find the value of the inverse chemical factor, $CaCO_3/CO_2$. 227

Compose a problem in which the *first* and another in which the *second* of these two factors is used as a multiplier in solving the problem.

32. Can chemical factors be treated as algebraic quantities? For example, what is the product of the factors Ca/CaO and $CaO/CaSO_4$? (A numerical result is not called for.)

33. Successive 5-gram samples of a sulfur-containing foodstuff yielded successive observed weights of barium sulfate. What number, used as a multiplier, will convert each of these weights into the percentage of sulfur in that sample? 275

Chapter 14

HOW IONS ARE FORMED

In dealing with crystals we first encountered *ions*—atoms or groups of atoms carrying electric charges. Then we found that the molecules of certain substances, hydrogen chloride for example, produce ions by reacting with water. But where do ions get their charges? Why do not oppositely charged ions, within a solution, immediately neutralize one another? Why are certain kinds of ions always charged positively and others always negatively? Why is the charge on certain ions exactly double or three times that on others? To answer these questions we must learn something about electricity.

► 173. Are There Atoms of Electricity?

The most significant thing we have learned about ions is that *their charges are always in the ratio of small whole numbers.* Thus the aluminum ion, Al^{+++}, has *three times*, and the magnesium ion, Mg^{++}, has *twice*, the charge on a sodium ion, Na^{+}. *Nowhere do we encounter a fraction of the charge on a sodium ion.* We therefore refer to this as a *unit positive charge.* The charge on a chloride ion, Cl^{-}, for the same reason, is referred to as a *unit negative charge.*

This certainly seems to indicate that electricity exists as indivisible *atoms of electricity*, which may attach themselves to ordinary atoms, giving them an electrical charge. But are these atoms of electricity of two different kinds, positive and negative, or is one kind of electricity merely the absence of the other? Are these atoms of electricity "pure electricity," or do they have some of the characteristics of ordinary atoms, for example a definite mass? The answers to these questions had to await the twentieth century, though they were suggested long before by some beautiful experiments, next described, on the passage of electricity through rarefied gases.

► 174. Experiments of Faraday and of Crookes

Air, under ordinary pressures, is a very poor conductor of electricity; but, when the pressure is reduced to a few millimeters or a fraction of a millimeter of mercury, air becomes a fair conductor. This may be demonstrated with a vacuum-discharge tube, shown in Fig. 75. When the terminals of an induction coil are connected with such a tube, a discharge of electricity takes place, which causes a part of the rarefied gas within the tube, adjacent to the negative electrode (cathode), to glow with light. As the pressure is still further diminished the "cathode glow" extends farther from the cathode, and at last,

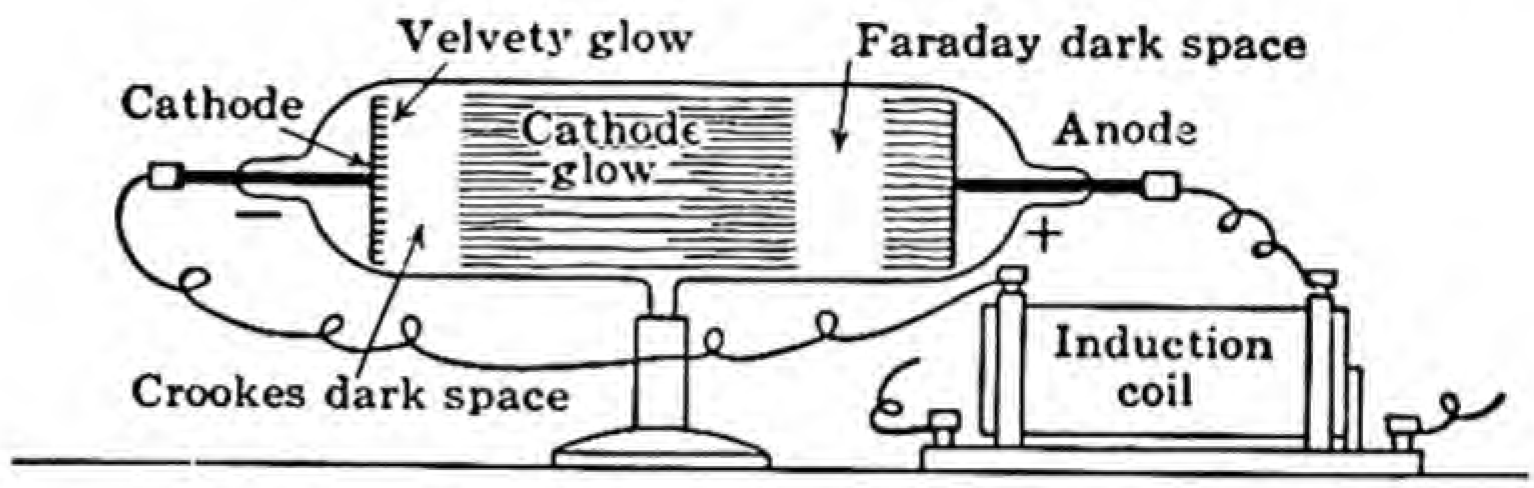


FIG. 75. Discharge of electricity through a rarefied gas.

under pressures of a few hundredths of a millimeter, may fill the whole tube. These facts were made familiar by Faraday more than a century ago (1836).

Another British physicist, Sir William Crookes (1879), pointed out some important characteristics of the discharge:

1. The discharge comes chiefly from the surface of the negatively charged electrode (*cathode*). It normally takes place in straight lines, but may be deflected or turned aside by a magnet, or by neighboring charges of electricity, carried by plates outside the tube.

2. A light paddle-wheel, placed in the path of the discharge, is caused to rotate in the same direction as it would if the cathode were emitting a stream of projectiles.

3. The glass walls of the tube, where the discharge from the cathode strikes the opposite end of the tube, *phosphoresce* brilliantly (emit visible light). Minerals placed within the tube, in the path of the discharge, also phosphoresce, in many instances displaying brilliant colors.

► 175. Cathode Particles

The fact that the cathode discharge is deflected by a magnet or by electrically charged plates seems to indicate that it cannot be a form of *radiant energy*, in other words, a variety of "invisible light." A beam of light would not be bent aside in any such manner, in traversing a

magnetic or electric field. Physicists were compelled to conclude that the discharge from the cathode (for a long time referred to as "cathode rays") must consist of a stream of particles of some sort, electrically charged. From the direction in which the rays were bent aside by a magnet it was evident that the particles composing them were charged negatively.

Were the cathode particles merely negatively charged atoms? Experiments showed this to be impossible. The discharge of cathode particles easily penetrated thin sheets of metals, and hence could be passed through a window of aluminum foil, into the air outside the tube. Then it traversed several millimeters or even several centimeters of air, under ordinary pressures. This observation seemed to indicate that the particles composing the rays were so small as to pass *between atoms*, or *through atoms*, without losing very much speed.

Next the cathode particles were shown to have a much smaller mass than that of the lightest known atom, an atom of hydrogen. Their charge, per unit of mass, proved to be enormous, in fact, hundreds of times as great as was ever observed for ions. Moreover, *they always had the same ratio of charge to mass, whatever material was used for the cathode, and whatever rarefied gas was contained in the tube.*

So here was something new in science—particles too small to be atoms, too light to be atoms, too heavily charged per unit mass to be atoms! They were seemingly identical, whatever their source. The conviction gradually grew that these cathode particles were really *atoms of negative electricity*, whose existence had long been foreseen from the fact that the charges on negative ions (Cl^-, SO_4^{--}, PO_4^{---}, etc.) are in the ratio of small whole numbers. They came to be called *electrons*.

176. Millikan Determines the Charge on an Electron

The first accurate measurements of the charge of a single electron were made by an American physicist, Robert Millikan (1909). He succeeded in giving microscopic oil droplets minute charges of electricity. Then he measured their rates of ascent or descent through air, under the combined action of the force of gravity and the electrical force exerted by two oppositely charged metallic places, in an evacuated chamber.

The charge carried by a single droplet could then be calculated. It was found always to be a *small whole multiple of a definite least charge*, which was taken to be the charge of an electron. This turned out to be an extraordinarily small quantity of electricity. If we had two metallic

plates 1 cm apart, in air, we would need to accumulate more than two thousand million electrons on each plate to create a repulsive force between them amounting to 1 dyne; and a dyne is a force that is hardly more than a fiftieth part of the weight of a postage stamp!

The charge of an electron having been determined, it was easy to calculate its mass, since the *ratio of charge to mass* has been accurately determined, by observing the deflection of streams of electrons in passing through electric and magnetic fields. It turned out that an electron, at low velocities, has about 1/1840 of the mass of a hydrogen atom, the lightest known material particle! This is so small a mass as to be neglected in comparison with that of the atoms taking part in chemical changes. The *charge* carried by the electron is its most important characteristic.

► 177. How Anions Are Formed

If the unit of negative electricity is the electron, then the charges of *anions* (negative ions) can be explained by assuming that the non-metallic atoms concerned *gain* one or more electrons. Thus a chlorine atom, gaining an electron, becomes a chloride ion:

$$Cl + e \rightarrow Cl^-$$

in which e stands for an electron; and an oxygen atom, gaining two electrons, becomes an oxide ion:

$$O + 2e \rightarrow O^{--}$$

Similarly for other *anions*. (Ex. 1, 2.)

178. The Photoelectric Effect

The elements that form *cations*, namely, the metals, have a strong tendency to lose electrons.

To demonstrate this, let a metallic ball (of brass or zinc, for example) be suspended by a silken thread. When *ultraviolet light* is permitted to fall upon it, it continuously loses negative electricity. If it was originally negatively charged, the charge is reduced, and often finally becomes positive. If it was originally electrically neutral, it becomes positively charged. But if it was originally positively charged, that charge either remains constant or increases up to a certain point. This loss of negative electricity (electrons) by metals and a few other materials, under the influence of visible or invisible light, is known as the *photoelectric effect*.

Certain metals lose negative electricity more readily than others. Those that do so most readily (rubidium and cesium) will do so even when ordinary visible light falls upon them. The rest require ultra-violet light, in other words, radiation of a higher *frequency* (p. 212). It is easy to show that the electricity lost is emitted as separate, individual electrons.

179. The Photoelectric Cell

A practical application of the effect just described is in the *photo-electric cell* (popularly called the "electric eye"). Cells having a sensitive surface of metallic cesium (or some other material that responds to

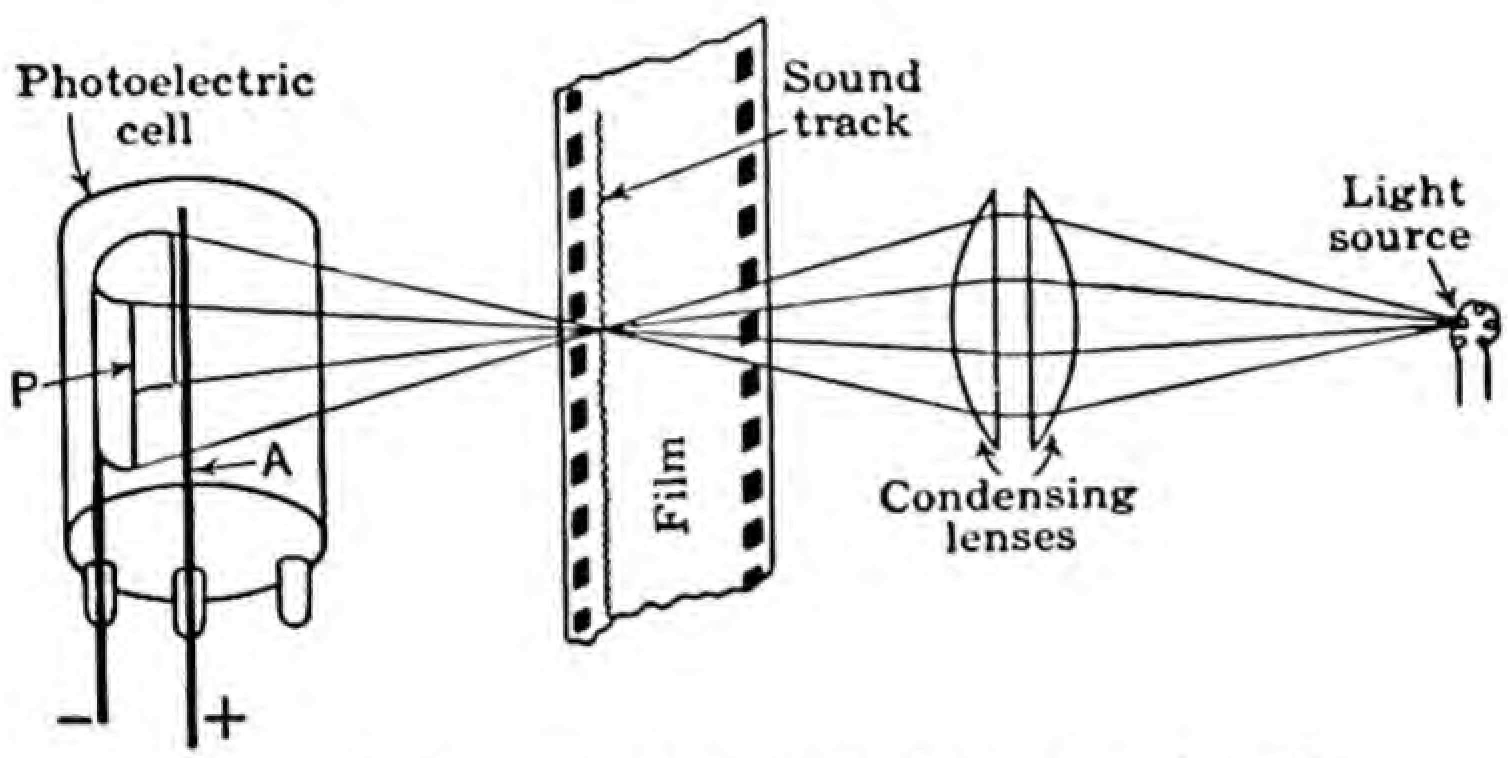


FIG. 76. Sound film and photoelectric cell.

visible light) have made sound films possible. The "sound track," a wavy black line at the edge of the film, intercepts the light beam falling into the photoelectric cell (Fig. 76). The intensity of the light entering the cell then varies with variations in the sound track. In consequence, the flow of negative electricity from the photosensitive surface, *P*, through the cell to the anode collecting wire, *A*, is made to vary continuously. This "photoelectric current" is amplified and made to actuate a loud speaker, thus reproducing the sound originally recorded on the film.

Other types of photoelectric cells may respond only to ultraviolet or infrared radiations, that is, to wavelengths that fail to affect the human eye. A multitude of interesting applications have been made, such as photoelectric cells that automatically count vehicles at traffic intersections; burglar alarms that sound when an intruder crosses an invisible beam of ultraviolet or infrared light; photoelectric controls that switch lights on and off automatically at one's approach.

Only metals emit electrons when visible light or ultraviolet light falls upon them. Non-metals fail to do this unless exposed to X-rays,

in other words, radiation of a frequency that is still greater than that of ultraviolet light.

180. Electrons Are Emitted by Heated Metals

All metals and many compounds (and indeed even non-metals) emit electrons when they are strongly heated. This is sometimes called the *thermionic effect.* The metals (Li, Na, K, Rb, Cs) that emit electrons freely at moderate temperatures are the very ones that emit them most readily under the influence of light. The rate of emission of electrons by heated metals increases rapidly with increasing temperature, just as the rate of evaporation of a liquid does.

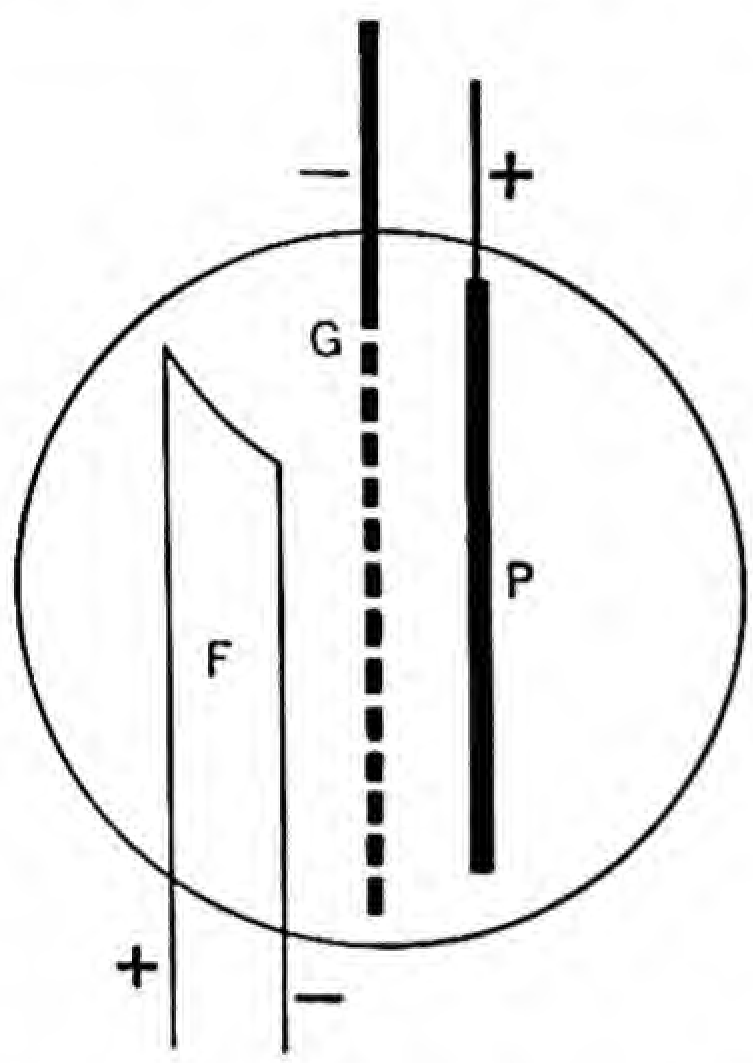


FIG. 77. A simple vacuum tube amplifier.

The loss of electrons by a heated metal is easily observed by anyone who uses glass-walled tubes in his radio set. Switch on the set and watch the filaments in the different tubes heat up. As soon as several have begun to glow the music (or advertising) comes on suddenly.

That such a filament really emits negative electricity is easily demonstrated as in Fig. 77. Between the heated *filament, F,* and the positively charged *plate, P,* is interposed a network or *grid, G.* If this grid is given a sufficiently strong negative charge the flow of electricity from filament to plate is interrupted. This shows that the filament must be emitting *negative* electricity as a stream of electrons, which are repelled by the negative charge on the grid.

The wireless signals that are received by the antenna ("aerial") of a radio set cause feeble currents in the antenna, which are carried to the grid, causing its charge to fluctuate, becoming alternately more and less negative, thousands or millions of times each second. In consequence, the flow of electrons from the filament toward the plate is greatly diminished or completely arrested, and then permitted to recontinue, thousands or millions of times each second. The wireless signal received upon the antenna thus controls a much larger flow of current, in the form of a stream of electrons within the tube. With several such tubes operating in a sequence, the feeble currents generated in the antenna by the incoming wireless signals may be stepped up sufficiently to operate a loud speaker.

► 181. How Cations Are Formed

The loss of electrons when light falls upon an insulated metal or when an insulated metal is heated always leaves the metal positively charged. This suggests that cations are formed in the same way, metallic atoms *losing electrons. Let us assume that each original (electrically neutral)* atom contains both positive and negative charges in equal numbers, but that for some reason only the negative charges (electrons) are removable. Then, if a silver atom should lose one of its electrons, what would remain would have a surplus positive charge of one unit, and so would be a positively charged silver ion:

Ag	$\rightarrow$	Ag^{+}	$+$	e
Neutral silver atom (containing + and − charges in equal numbers)	*Yields* or *produces*	Silver ion (a silver atom containing a surplus of one + charge)		A single negative charge, *i.e.*, an *electron*

Similarly, if an atom of zinc should lose two electrons, it would be left with a surplus positive charge of two units, and if an atom of aluminum should lose three electrons it would be left with a surplus positive charge of three units:

Zn	$\rightarrow$	$Zn^{++} + 2e$
Zinc atom		Zinc ion
Al	$\rightarrow$	$Al^{+++} + 3e$
Aluminum atom		Aluminum ion

This explanation of how cations acquire their charges is rendered the more plausible by the observation that the metals which lose electrons most readily when heated, or under the influence of light, are the very ones that most readily form cations. (Ex. 3–7.)

► 182. Avogadro's Number

Let us hang two silver plates in a solution of a silver salt and pass an electric current through it. Metallic silver is continuously deposited at the negative electrode (cathode). We assume that electrons, coming from the *generator* or storage cell, combine with silver ions at the surface of the cathode, to form electrically neutral silver atoms:

Ag^{+}	$+$	e	$\rightarrow$	Ag
Silver ion (dissolved)		Electron (from generator)		Atom of metallic silver (deposited on surface of cathode)

Each electron arriving at the cathode contributes its own tiny portion of negative electricity and causes one atom of silver to be

deposited. So, atom by atom, during a period of some hours, we may deposit a considerable weight of silver.

The experiment may be arranged as shown in Fig. 78. The milliammeter, read at frequent intervals, enables one to determine the total quantity of electricity passed through the cell. If this is divided by the charge carried by a single electron (§ 176) we get the number of electrons passed. Each electron causes one atom of silver to be deposited; hence the total number of electrons is also the total number of *atoms* deposited.

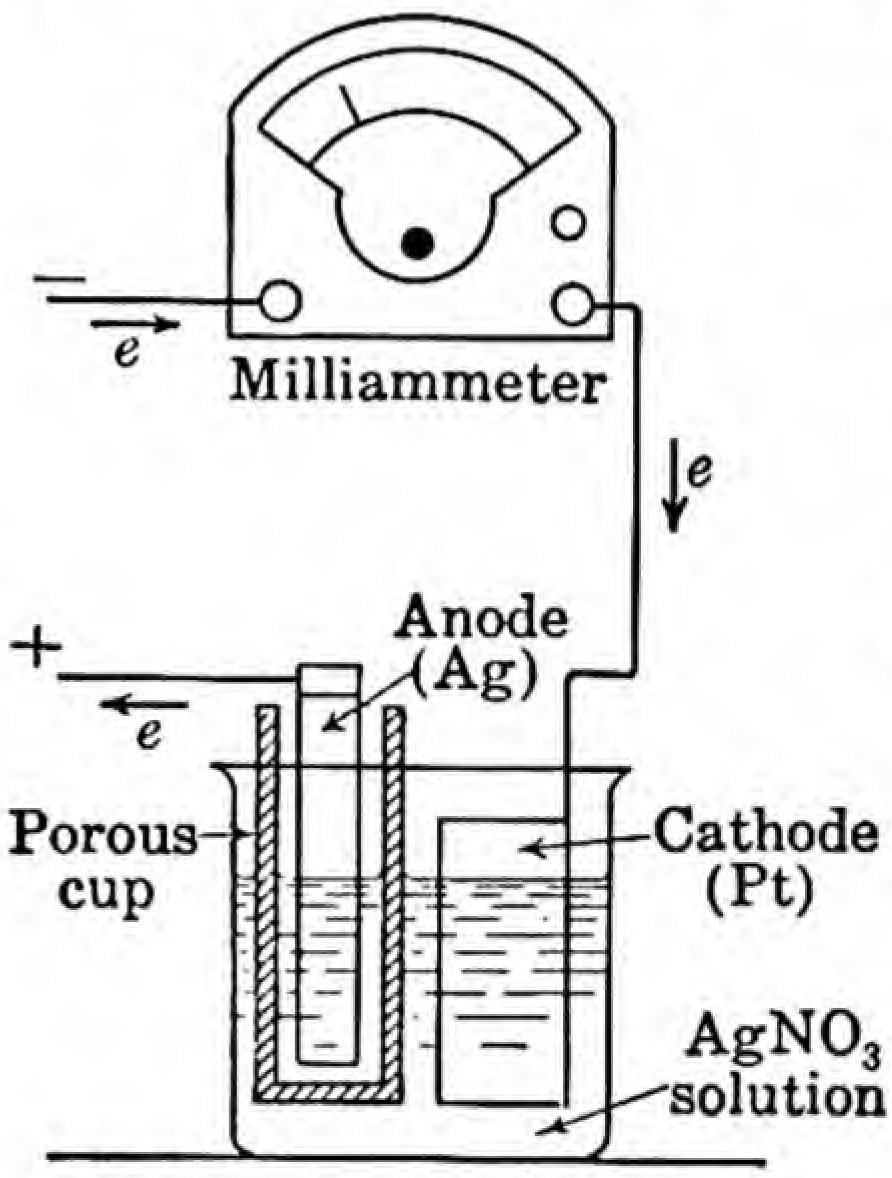


FIG. 78. Deposition of metallic silver on cathode in a silver coulometer.

It turns out that 1 gram atom (107.88 grams) of silver contains 6.02×10^{23} atoms—somewhat more than the number represented by 6, followed by 23 zeros!

Now a gram atom is a quantity that is large or small, in proportion to the weight of a single atom of the element concerned (§ 115). So, if it takes 6.02×10^{23} atoms to make a gram atom of silver it will take that many atoms to make a gram atom of any other element.

The number 6.02×10^{23} is called *Avogadro's number* (in honor of the chemist who first showed how molecular weights and hence how atomic weights may be derived, § 33). It represents *the number of atoms in a gram atom, the number of molecules in a gram molecule (mole), and the number of ions in a gram ion of any material (gas, liquid, or solid).* (Ex. 8.)

Avogadro's number is one of the fundamental constants of nature. Its value has been most accurately deduced in the manner just shown, from the charge of an electron, as determined by Millikan and others. It has been confirmed in many independent ways, for example, by calculations based on the rate at which radium salts emit helium (§ 578) or the rate of scattering of slowly settling heavy particles, suspended in a gas or liquid (§ 430). It has even been roughly computed from the colors of the sunset sky! *With its aid we can calculate not merely the relative weights of atoms* (as in § 33) *but also their actual individual weights.* (Ex. 9–13; use a rounded value, 6×10^{23}, for Avogadro's number.)

► 183. Electrons Contrasted with Ions

It is important for the student to distinguish sharply between the two kinds of electrically charged particles with which we have had to deal. To repeat and summarize what we have said:

Electrons are unit *negative* charges of electricity. They are of negligible mass or weight in comparison with ordinary atoms and molecules. We use the symbol *e* to represent an electron.

Ions are electrically charged atoms or groups of atoms, acting as electrically charged molecules. Some are charged positively and others negatively. The charge of an ion is always a small whole multiple of the charge of an electron. The lightest ion, namely, the proton, H^+, has about 1840 times the mass of an electron.

The mass or weight of an ion is that of the atoms that compose it, since the small number of electrons gained or lost in producing the charge on an ion is not sufficient to affect its mass or weight perceptibly. (Ex. 14–16.)

We have accounted for the charges on ions by assuming that atoms of metallic elements tend to lose electrons and those of non-metallic elements tend to gain electrons. We have had to assume that every atom contains both positive and negative charges of electricity, but that ordinarily only negative charges are ever lost or gained by an atom. Immediately one asks why. Moreover, if every atom contains both positive and negative charges of electricity, why do these not neutralize one another? Why do atoms of metals commonly tend to lose electrons, whereas those of non-metals tend to gain electrons? These are fundamental questions, whose answers in later chapters will carry us far in explaining what actually happens in chemical reactions, and why different sorts of atoms combine in the proportions that they do, in forming molecules.

Technical Words

Phosphorescence—the emission of visible light (1) by living organisms (molds, bacteria, insects, fish); or (2) as the result of bombardment by swiftly moving electrons or material particles; or (3) with *phosphorescent minerals*, as the result of previous exposure to light.

Cathode rays—a name formerly given to streams of electrons, emitted by the cathode in the discharge of electricity through rarefied gases.

Electron—an apparently indivisible ultimate negative charge of electricity, of nearly negligible mass in comparison with atoms or ions.

Photoelectric effect—the emission of electrons (usually by a metal) under the influence of radiant energy (light, visible or invisible).

Ultraviolet light—light having a frequency (p. 212) that is just higher than that of ordinary visible light.

Photoelectric cell—an instrument (p. 207) in which a minute electric current is produced by the emission of electrons from a metallic plate, under the influence of light.

Thermionic effect—the emission of electrons by certain materials at high temperatures. Metals and metallic oxides are good examples.

Induction coil (pictured in Fig. 75)—a device for obtaining an alternating electric current, usually delivered at a high potential (high "voltage").

Generator (colloquially called a "dynamo")—any device for setting up a flow of electricity by the expenditure of mechanical energy (for example, by rotating coils of wire in a magnetic field).

Coulometer—an instrument for measuring the quantity of electricity that passes through a circuit by the quantity of chemical change that the current induces (for example, by the weight of a metal that it deposits on the cathode or the volume of gas that it liberates).

Avogadro's number, p. 210.

Cosmic rays—very penetrating radiation of unexplained origin and nature, which reaches the earth, apparently from outer space. It appears not to be radiant energy, but is a complex phenomenon, including swift-moving electrons and the products that result from impact of these on the molecules of the gases of the earth's atmosphere.

Frequency—the number of complete vibrations per second in the electromagnetic wave that accompanies a beam of light. When all the light emitted by a source of light is of the same frequency the beam is said to be *monochromatic.*

Summary

► § 173. A significant fact about the charges of ions, in comparison with one another. What this seems to indicate.

► § 174. The conductivity of air or electricity, under ordinary and very low pressures.

What the "negative glow" is, when electricity is discharged through a gas under low pressures.

Which electrode chiefly emits the discharge. A mechanical effect and an optical effect produced by the discharge.

► § 175. How it was proved that the cathode discharge, in the experiment just described, is not a form of radiant energy.

How it was determined whether the cathode rays were negatively or positively charged.

Evidence that the particles were of very small size. Final conclusion concerning their nature. Name since given them.

► § 176. What was actually measured in Millikan's experiment. Forces acting on the microscopic droplets. What this experiment proves with regard to the charge carried by a single droplet. Conclusion.

How the ratio of charge to mass has been determined for an electron. How the mass of an electron compares with that of a hydrogen atom.

► § 177. How anions are formed. An equation to illustrate.

§ 178. A name given to the emission of electrons under the influence of light. What determines whether ordinary visible light will cause a metal to emit electrons, or whether ultraviolet light is needed.

§ 179. A sketch and explanation of how the sound track at the edge of a moving-picture film is made to reproduce the sound.

Several other applications of the photoelectric cell.

§ 180. A sketch and explanation of what happens within the vacuum tube of a radio set when the filament is heated. How this phenomenon is applied in radio reception.

Name given to the emission of electrons by many materials at high temperatures. Which metals emit electrons most readily under the influence of light or when heated.

How the rate of emission of electrons is affected by increasing the temperature.

► § 181. Which metals form cations most readily and what conclusion is drawn from this fact. An explanation of how cations acquire their charges.

► § 182. Description of an experiment in which we deduce the number of atoms of silver in a gram atom of that element. (Show the steps in the reasoning.)

Name given the number thus derived. How we know that it represents the number of atoms in a gram atom, for *any* element. What else it represents. Two other methods for determining it.

► § 183. How electrons compare with ions in charge and mass.

Exercises

1. Write an equation to show that a molecule of chlorine, in accepting two electrons, produces two chloride ions.

2. Write an equation to show that two oxide ions, if compelled to lose electrons, produce a molecule of oxygen gas.

3. Write equations to show the manner in which metallic iron, by loss of electrons, may form either a ferrous or a ferric ion.

4. Write equations to show that protons, by being compelled to accept electrons, may be discharged as hydrogen gas.

5. Write an ionic equation to show that metallic zinc, reacting with a cupric salt (*i.e.*, cupric ion), produces metallic copper and a zinc salt (*i.e.*, zinc ion).

Which element gains and which loses electrons in this reaction.

6. Write an equation to show how a ferric salt (*i.e.*, ferric ion), by being compelled to accept electrons, may be converted into a ferrous salt.

7. Write an equation to show the gain or loss of electrons that must occur when a cupric salt, Cu^{++}, is converted into a cuprous salt, Cu^{+}.

8. A mole of a certain substance is divided equally among all the inhabitants of the earth (estimated at 1500 millions). How many molecules does each person receive? With molecules valued at a thousand million for a cent, what is your share worth? (Use powers of 10, Appendix E.) 4×

9. What is a milligram atom? How many actual atoms are there in a milligram atom of any element? 6×

10. What is the actual weight in grams of one atom of mercury expressed as a power of 10? 3×

11. What is the weight in grams of a gram atom of magnesium? Calculate, roughly, the weight (expressed as a power of 10) of a single atom of magnesium. 240, 4×

12. About what volume, under standard conditions, is occupied by 6×10^{23} molecules of any gas? Calculate roughly the number of molecules in each cubic centimeter of a gas, under standard conditions. 224, 2.7×

13. A powerful vacuum pump is able to reduce the air within a vessel to a millionth of an atmosphere of pressure. From the result of the preceding problem, how many molecules of air must still be present, at 0°C, in each cubic centimeter of the near-vacuum which this pump produces? 2.7×

14. How many grams in a gram ion of nitrate ion? 620

15. Use Avogadro's number to calculate the weight in grams (expressed as a negative power of 10) of a single hydrogen atom. 1.66×

16. From the result of the preceding problem calculate the weight in grams of a single electron. 9×

Chapter 15

PROPERTIES OF ACIDS

► 184. The Reactions of Acids

Now that we have acquired some skill in writing formulas, let us consider the reactions of acids. Acids react with and are neutralized by:

1. *Metallic hydroxides*, forming a salt and water:

$$NaOH + HCl \rightarrow NaCl + H_2O$$

$$\left.\begin{array}{ll} NaOH + H_2SO_4 \rightarrow \underset{\text{Sodium hydrogen sulfate}}{NaHSO_4} + H_2O & \text{(First stage)} \\ NaOH + NaHSO_4 \rightarrow \underset{\text{Sodium sulfate}}{Na_2SO_4} + H_2O & \text{(Second stage)} \end{array}\right\}$$

2. *Metallic oxides*, forming a salt and water:

$$ZnO + 2HCl \rightarrow \underset{\text{Zinc chloride}}{ZnCl_2} + H_2O$$

3. *Sulfides*, forming a salt and liberating hydrogen sulfide gas;

$$ZnS + 2HCl \rightarrow ZnCl_2 + H_2S \uparrow$$

Observe how similar this is to the preceding reaction, S merely replacing O.

4. *Carbonates* and *sulfites*, forming a salt and liberating carbon dioxide or sulfur dioxide gas:

$$Na_2CO_3 + 2H_2SO_4 \rightarrow \underset{\text{Sodium hydrogen sulfate}}{2NaHSO_4} + H_2CO_3 \hookrightarrow H_2O + CO_2 \uparrow$$

$$Na_2SO_3 + 2H_2SO_4 \rightarrow 2NaHSO_4 + H_2SO_3 \hookrightarrow H_2O + SO_2 \uparrow$$

We have represented these reactions as first forming carbonic or sulfurous acid, which then decomposes, reversibly, but nearly completely, liberating a gas. This is a convenience in remembering what is pro-

duced, though the reaction probably does not take place in two separate steps.

5. Many metals, forming a salt and liberating hydrogen gas:

$$Zn + 2HCl \rightarrow \underset{\text{Zinc chloride}}{ZnCl_2} + H_2 \uparrow$$

Not all metals react with acids, and when they do the gas evolved is not always hydrogen (§ 88).

In all five of the preceding reactions a solution is obtained that contains a dissolved *salt* whose formula may be derived by replacing part or all of the hydrogen in the formula of the acid by one or more atoms of a metal. In some instances this salt can be recovered in crystalline form, merely by evaporating the solution. In others, evaporation chemically alters the salt, for reasons to be mentioned later (§ 396). (Ex. 1–8.)

► 185. Active and Slightly Active Acids

Certain acids are much *stronger* or *more active* than others. To compare different acids with regard to activity or strength we must be sure that we are comparing solutions of *equivalent concentration*, in other words, solutions such that equal volumes react with and are neutralized by the same weight of a base. The strongest or most active of the acids compared will be found (1) to *taste most sour*, (2) to *affect indicators* (such as litmus) *the most intensely*, (3) *to react the most rapidly*, as a rule, with metals and insoluble carbonates, (4) to *react most nearly completely with slightly active bases*, such as ammonium hydroxide. Of these four tests the last is by far the most important.

It turns out that *the most active acids, when dissolved in water, do not differ greatly in activity*. The student will find it helpful to remember how some of the most common acids are classified in the following table. Acids not named are those whose names are assumed to have been made familiar in Chapter 13.

Classification of Acids According to Strength or Activity

Percentages represent apparent degree of ionization (§ 190) in tenth-normal solution (§ 294) in water.

Active						*Moderately Active*		
HCl	HBr	HI	HNO_3	$HClO_4$	H_2SO_4	$H_2C_2O_4$	H_2SO_3	H_3PO_4
				Perchloric acid	85%	50%	33%	27%
100%								

Slightly Active			*Very Slightly Active*		
HF	HNO_2	$HC_2H_3O_2$	H_2CO_3	H_2S	HCN
8.5%	Nitrous acid 6.5%	1.3%	0.17%	0.07%	0.01%

► 186. Acids React with the Solvent in Being Dissolved

The activity of an acid depends a great deal on the *solvent* in which it is dissolved—whether dissolved in water, for example, or in dry ether or benzene. Moreover, when a slightly active acid is diluted with water its activity does not fall off as much as one would expect: Acetic acid, when diluted with water to make a 5 per cent solution, has actually about *half* the activity that it does in a 20 per cent solution, instead of only one-fourth that activity.

All this makes it appear that *activity may be altered by a reaction between the acid and the solvent*, in dissolving the acid or in diluting the solution with a further quantity of solvent. Evidence for such a reaction is found in the considerable amount of heat that is liberated when hydrogen chloride gas is dissolved in water or when concentrated sulfuric acid is diluted with water. The solution formed, in either case, is found to be a good conductor of electricity, though the pure substances which we represent by the formulas HCl and H_2SO_4 are poor conductors. This convinces us (§ 142) that *the reaction between acid and water produces ions.*

For a long time, chemists assumed that the water in some manner acted as a catalyst, causing the acid, in the act of being dissolved, to be *dissociated* (reversibly decomposed) into ions:

$$HCl \rightarrow H^+ + Cl^-$$

The hydrogen ion was inferred to be positively charged from the fact that it moved toward the *negative electrode*, and was there liberated as hydrogen gas, whenever an acid electric current was passed through a solution of hydrochloric acid. The chloride ion, for the opposite reason, was inferred to be negatively charged.

However, there are reasons for believing that the positively charged hydrogen ion, H^+, generally called a *proton*, normally exists in combination with something else. So the reaction of hydrogen chloride with water (shown in Fig. 79) is now written:

$$\underbrace{HCl \quad + \quad H_2O}_{H^+\text{ (transferred)}} \quad \rightarrow \quad \underbrace{\underset{\text{Oxonium ions}}{H_3O^+} \quad + \quad \underset{\text{Chloride ions}}{Cl^-}}_{\text{Hydrochloric acid}}$$

In this reaction, *a proton is transferred from each molecule of hydrogen chloride to a molecule of water.* The original molecule of hydrogen chloride was electrically neutral because it contained equal quantities of positive and negative electricity; so, in losing a positively charged proton, it must leave behind a negatively charged residue, the chloride ion, Cl^-.

The positively charged ion, H_3O^+, formed by a proton combining with water, is often referred to as *hydrogen ion.* It is also often termed

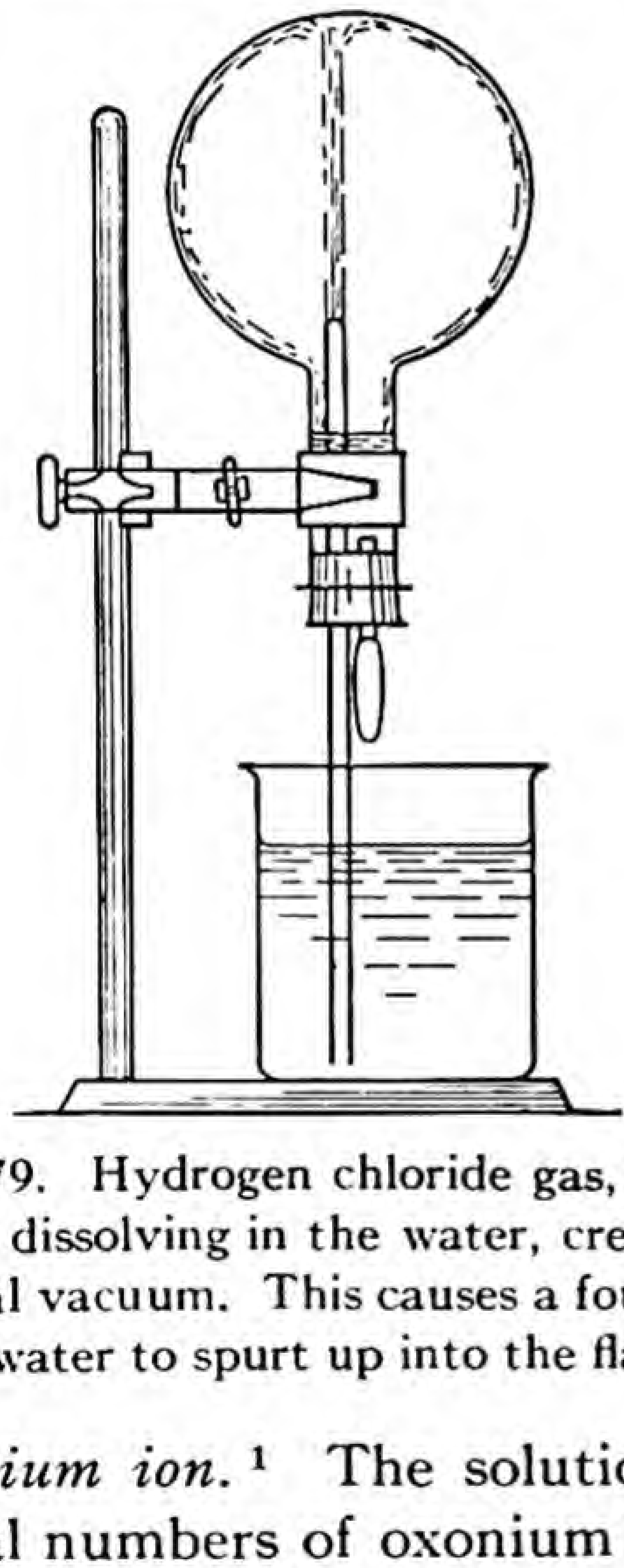


FIG. 79. Hydrogen chloride gas, in the flask, dissolving in the water, creates a partial vacuum. This causes a fountain of water to spurt up into the flask.

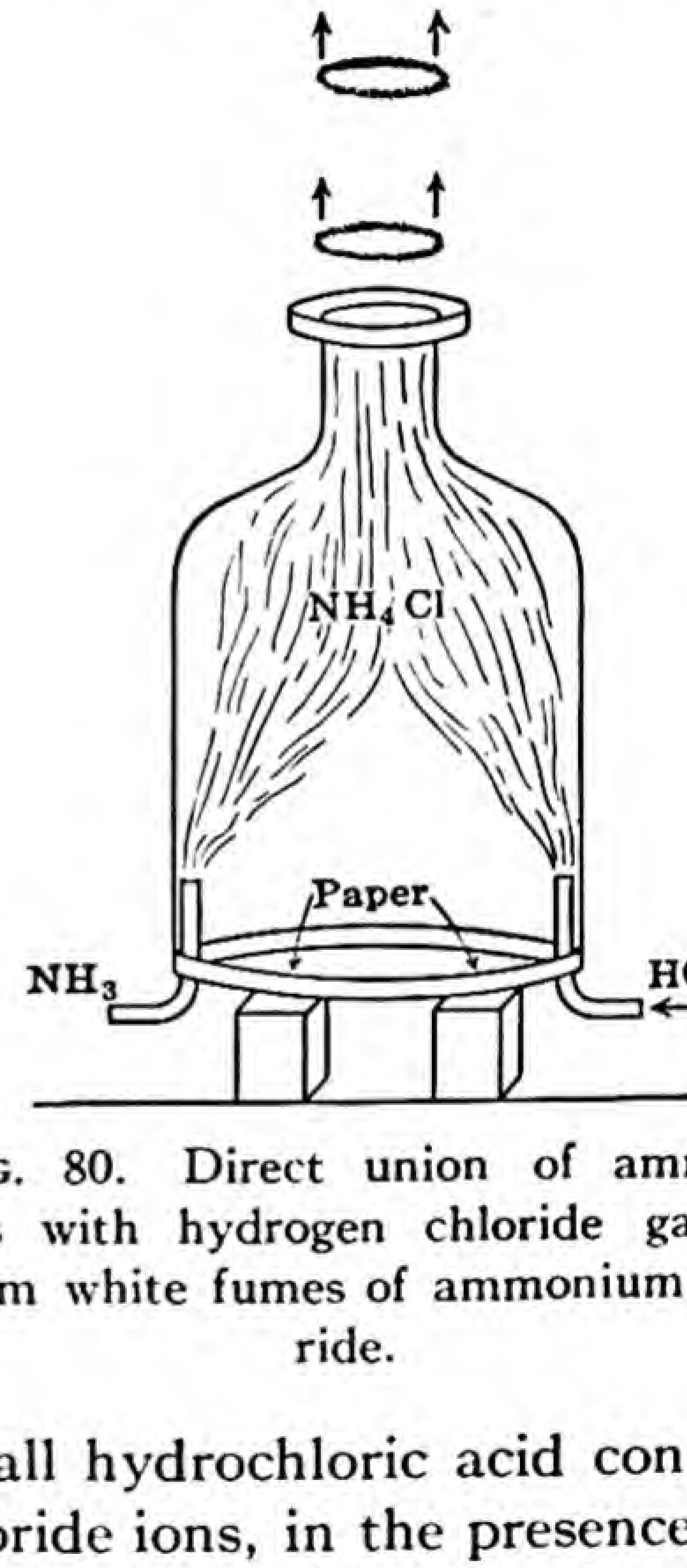


FIG. 80. Direct union of ammonia gas with hydrogen chloride gas, to form white fumes of ammonium chloride.

oxonium ion.[1] The solution that we call hydrochloric acid contains equal numbers of oxonium ions and chloride ions, in the presence of a surplus of ordinary water molecules. For this reason it might also be termed oxonium chloride.

The reaction just considered should be compared with that between hydrogen chloride gas and ammonia gas. When these two gases come in contact they react to form dense white fumes of ammonium chloride (Fig. 80):

$$\underbrace{HCl \quad + \quad NH_3}_{H^+ \text{ (transferred)}} \quad \rightarrow \quad \underbrace{\underset{\text{Ammonium ions}}{NH_4^+} \quad + \quad \underset{\text{Chloride ions}}{Cl^-}}_{\text{Ammonium chloride}}$$

[1] The only difference between these two terms is that the former (hydrogen ion) is a little the more general, and refers to a proton in combination with any solvent with which it will combine.

Here we have a contest for protons between Cl^- and NH_3. The latter wins, combines with an additional proton, and thus is converted into the ammonium ion, NH_4^+, setting free the chloride ion, Cl^-.

By tapping the paper diaphragm at the bottom of the cylinder (Fig. 80) the white fumes may be ejected at the top as a succession of smoke rings, which may readily be mistaken for a gas or vapor. They really consist of a multitude of microscopic crystals of ammonium chloride. (Ex. 9.)

► 187. Complete vs. Incomplete Reaction with Water

Whenever an *active* acid reacts with water the solution obtained is such a good conductor of electricity that we seem justified in believing that *all* the acid molecules are converted into ions. The reaction of hydrogen chloride with water has furnished a good example. Another is seen in the reaction that takes place in dissolving hydrogen nitrate (the pure substance whose solution is termed nitric acid):

$$\underbrace{\underset{\text{Hydrogen nitrate}}{HNO_3} \quad + \quad H_2O}_{H^+ \text{ (transferred)}} \quad \rightarrow \quad \underbrace{\underset{\text{Oxonium ion}}{H_3O^+} \quad + \quad \underset{\text{Nitrate ion}}{NO_3^-}}_{\text{Nitric acid}}$$

But when a *slightly active* acid reacts with water the reaction remains incomplete because it is *reversible*. An example is furnished by the reaction of acetic acid with water:

$$\overbrace{\underset{\substack{\text{Acetic acid}\\\text{molecules}}}{HC_2H_3O_2} \quad + \quad \underset{\substack{\text{Water}\\\text{molecules}}}{H_2O}}^{H^+ \text{ (transferred)}} \quad \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \quad \underbrace{\overset{\substack{\text{Acetate}\\\text{ions}}}{C_2H_3O_2^-} \quad + \quad \overset{\substack{\text{Oxonium}\\\text{ions}}}{H_3O^+}}_{H^+ \text{ (transferred)}}$$

The double arrow indicates that we have to do with two reactions that proceed at the same rate in opposite directions, thus giving us another example of *chemical equilibrium* (§ 63). But the lighter arrow points toward the right. This is a device for indicating that the left-to-right reaction (*a*) does not proceed very far before the opposing reaction (*b*) proceeds at an equal rate. From that moment onward, each reaction exactly cancels the work of the other, hence both reactions remain forever incomplete. Unless very greatly diluted, the acetic acid in a solution of that substance in water exists chiefly as acetic acid molecules, $HC_2H_3O_2$, rather than as ions.

The important thing to remember, then, is that *slightly active acids are only very incompletely converted into ions in being dissolved in anything short of an infinite amount of water.* This might be the

more forcibly indicated if we should write

$$HC_2H_3O_2 + H_2O \rightleftharpoons {\scriptstyle H_3O^+ + C_2H_3O_2^-}$$

using large and small type to represent large and small quantities of material, at equilibrium, but using identical arrows in the two directions to indicate that the oppositely directed reactions proceed at the same rate. (Ex. 10.)

► 188. Active Acids Are Weak Proton Retainers

The reactions just considered show very plainly what the real difference is between active and slightly active acids. Active or "strong" acids are merely *weak proton retainers*. This is as if we should rate as active philanthropists all persons unable to withstand an appeal for charity. Dissolve an active acid in water and *all* its molecules yield protons to the water.

A slightly active or "weak" acid, on the other hand, is a *strong proton retainer*. It holds its protons so strongly that very few acid molecules can transfer their protons to water before this reaction is offset by one of the opposite sort. But diluting the solution with more and more water increases the rate of transfer of protons from acid molecules to water molecules. So even acetic acid finally approaches complete conversion into ions, as a solution of it in water is indefinitely diluted (in other words, approaches *infinite dilution*).

189. Ionization in Successive Stages

A molecule of sulfuric acid contains two hydrogen atoms, hence the transfer of protons to water takes place in two separate stages. The *first stage* is fairly complete, as may be indicated by using a heavy arrow for the left-to-right reaction (*a*) in the equation:

H⁺ (transferred)

$$\underset{\text{Hydrogen sulfate}}{H_2SO_4} + H_2O \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \underbrace{\underset{\text{Oxonium ions}}{H_3O^+} + \underset{\text{Hydrogen sulfate ions}}{HSO_4^-}}_{\text{Sulfuric acid of moderate concentration}}$$

A few of the hydrogen sulfate ions produced in the first stage transfer their protons to water and are converted into sulfate ions in a *second stage:*

H⁺ (transferred)

$$\underset{\text{Hydrogen sulfate ions}}{HSO_4^-} + H_2O \rightleftharpoons \underbrace{\underset{\text{Oxonium ions}}{H_3O^+} + \underset{\text{Sulfate ions}}{SO_4^{--}}}_{\text{Very dilute sulfuric acid}}$$

So we see that sulfuric acid behaves like a mixture of two different acids. The first, H_2SO_4, is fairly active. The second, an anion acid, HSO_3^-, is only very slightly active. If we ask what particles are present in a dilute solution of sulfuric acid, the answer is that ordinary water molecules, H_2O, are the most plentiful. Hydrogen ions (oxonium ions), H_3O^+, are next most plentiful, since they are produced in both the reactions of *ionization* (ion formation). Almost as plentiful are hydrogen sulfate ions, HSO_4^-, produced in the fairly complete first stage of ionization; and least plentiful are sulfate ions, SO_4^{--}, since these are formed only in the second stage, which is relatively incomplete. (Ex. 11.)

The ionization of sulfurous acid, H_2SO_3, or oxalic acid, $H_2C_2O_4$, is accomplished in two stages, as just described for sulfuric acid, except that these two acids are only moderately active, hence the first stage of ionization is only moderately complete. Phosphoric acid, H_3PO_4, ionizes in three successive stages, the first only moderately complete and each of the others much less complete than the preceding stage. (Ex. 12.)

190. Degree of Ionization

The stronger or more active an acid the greater proportion of its molecules transfer protons to water (or to any other solvent) before equilibrium is reached, hence the greater the proportion of molecules converted into ions. By the *degree of ionization* we mean the fractional part of all the acid molecules which are converted into ions, *under the assumption that no intermediate condition exists between the molecular condition and the ionic condition.*

Ignoring this difficulty in defining or measuring the degree of ionization we may nevertheless estimate the *apparent* degree of ionization of an acid, in a solution of specified concentration, from its conductivity and in other ways. Hydrochloric acid, or any other very active acid, in a solution in water behaves as if practically completely converted into ions. Its apparent degree of ionization is 100 per cent. Acids that are only moderately or slightly active have a lower apparent degree of ionization, as shown in the table on pp. 216, 217. As such an acid is more and more diluted with water, the increasing proportion of water increases the number of acid molecules which transfer a proton to water, hence increases the apparent degree of ionization. We shall learn more about this in a later chapter (§ 409).

► 191. Generalized Equations for the Reactions of Acids

If we are using a dilute solution of an active acid in water, in any typical acid reaction, we may be sure that it is oxonium ion, H_3O^+, that serves as the "acid." But if we use a moderately or slightly active acid we cannot quite be sure whether acid molecules or oxonium ions are responsible for the reaction. Very probably both. Since we are so often in doubt whether the proton shifted in a reaction comes from *acid molecules* or from *oxonium ions*, we shall use H^+, properly the symbol of a proton itself, as a *generalized symbol for an acid*, and shall employ H_3O^+ *only when we wish to emphasize that the proton of the acid has first been transferred to water, before being handed on to something else.*

The typical reactions of acids (§ 184) then all take very simple forms:

1. Reaction with a metallic *hydroxide* (alkali):

$$\underset{\text{Any acid}}{H^+} + \underset{\text{Any metallic hydroxide}}{OH^-} \rightarrow H_2O$$

Observe that *the sole product appears to be water.* Yet the metallic hydroxide also yields a cation, and the acid yields an anion, which together will produce a salt. For this reason, an acid reacting with a metallic hydroxide always yields not only water, but also a salt.

2. Reaction with a *metallic oxide:*

$$\underset{\text{Any acid}}{2H^+} + \underset{\text{Any metallic oxide}}{O^{--}} \rightarrow H_2O$$

Here again, the reaction produces a salt, not shown by the equation. The same is true of the next two cases.

3. Reaction with a *sulfide:*

$$2H^+ + S^{--} \rightarrow H_2S\uparrow$$

4. Reaction with a *carbonate* or *sulfite:*

$$2H^+ + CO_3^{--} \rightarrow H_2O + CO_2\uparrow$$

$$2H^+ + SO_3^{--} \rightarrow H_2O + SO_2\uparrow$$

5. Reaction with a *metal:*

$$2H^+ + \underset{\text{Metallic sodium}}{2Na} \rightarrow \underset{\text{A sodium salt}}{2Na^+} + H_2\uparrow$$

$$2H^+ + \underset{\text{Metallic magnesium}}{Mg} \rightarrow \underset{\text{A magnesium salt}}{Mg^{++}} + H_2\uparrow$$

Observe that Na and Mg refer to these elements in the free, uncombined, or "metallic" state; by contrast, Na^+ and Mg^{++} refer to *chemically altered* sodium and magnesium, as encountered in sodium and magnesium compounds. *Students who neglect to think clearly about this, or who are not careful to indicate charges carried by ions, will soon cease to make progress.* (Ex. 13–16.)

The above *generalized equations*, otherwise called *ionic equations*, have the merit of being simple, and of concentrating on what is most essential in each reaction. Yet the moment we enter the laboratory, we realize their chief shortcoming: We cannot work with "any acid" and "any hydroxide"—we must make a choice. As soon as we do that we get back to the *conventional equations* of § 184. These must be employed whenever we need to make a calculation involving the actual weights or volumes of the reactants weighed out for a reaction or the resultants produced from it. This is for the simple reason that one can never weigh any ionic substance separately from another of opposite charge. Furthermore, a conventional or specialized equation definitely indicates what salt is produced, in instances in which an ionic equation ignores the salt completely.

► 192. Bases

The word **base** was originally applied to any substance that was capable of neutralizing an acid. Then it tended to be limited to *metallic hydroxides* (or, in some applications, to these and *metallic oxides*). *This is still the most common usage of the word base.*

However, since acids have come to be recognized as *proton donors*, chemists are tending to broaden their use of the word base, until with many it has come to mean any *proton acceptor*. In the reactions of the preceding page they would recognize as bases:

OH^-	O^{--}	S^{--}	CO_3^{--}	SO_3^{--}
Hydroxyl ion "Any metallic hydroxide"	Oxide ion "Any metallic oxide"	Sulfide ion "Any sulfide"	Carbonate ion "Any carbonate"	Sulfite ion "Any sulfite"

since each of these ions combines with one or two protons, in reacting with an acid.

But the last of the typical reactions of acids, listed on the preceding page, namely the reaction of acids with metals, is of a very different nature. Instead of the acid transferring protons to the metal, *electrons* are transferred from metal to acid. The protons of the acid, by accepting electrons from the metallic atoms, are converted into elec-

trically neutral hydrogen atoms, which combine in pairs to form molecules of hydrogen gas:

$$\underbrace{2H^+ \quad + \quad \overset{\text{Metallic sodium}}{2Na}}_{2e\text{ (transferred)}} \quad \rightarrow \quad \overset{\text{A sodium salt}}{2Na^+} \quad + \quad H_2\uparrow$$

$$\underbrace{2H^+ \quad + \quad \overset{\text{Metallic magnesium}}{Mg}}_{2e\text{ (transferred)}} \quad \rightarrow \quad \overset{\text{A magnesium salt}}{Mg^{++}} \quad + \quad H_2\uparrow$$

Observe that metallic atoms, in each case, by losing electrons, are converted into positively charged ions (cations) of a salt.

So it is evident that metals are not regarded as bases by persons who define bases as proton acceptors. But metals do neutralize acids, (in the sense that they cause acids to be transformed into salts), hence they were originally classed as bases and are beginning once more to be so regarded, by some chemists.

Then a base is a *metallic hydroxide*, a *proton acceptor*, or an *acid neutralizer*, according to the textbook or journal article that you happen to be reading. This confusion will probably continue for years, in spite of the efforts of champions of particular points of view to win acceptance for their own definitions. Fortunately, it is usually easy to determine what meaning an author has in mind, when he uses the word base. In this book, to avoid all chance of misunderstanding, a *metallic hydroxide* will be called that, rather than merely a "base."

Metallic hydroxides are actually of two kinds:

1. *Hydroxides of the alkali and alkaline-earth metals* (jointly termed light metals, § 213) are usually termed *alkalies* or *caustic alkalies.* Examples are NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$. Except for magnesium hydroxide, $Mg(OH)_2$, which is only very slightly soluble and but slightly active, the alkalies are *readily or at least fairly soluble* and are *active bases.* Like most salts, they are *ionic compounds.* Whether in solid form or dissolved in water, they exist chiefly as ions (Na^+ and OH^-, for example), rather than as molecules.

2. *Hydroxides of the heavy metals* are better termed *hydrous oxides.* They are *practically insoluble,* slimy, gelatinous compounds, which are said to be *hydrous* because they contain a variable and indefinite amount of water. They are commonly represented by such formulas

as $Zn(OH)_2$, $Fe(OH)_3$, which ignore the surplus water that they contain; but most of them, by loss of water in a dry atmosphere, may be converted into oxides, without any halt or delay at the stage of hydration that corresponds to the formulas assigned them. (Ex. 17, 18.)

Observe that the hydrous oxides, unlike the alkalies, are non-ionic compounds.

193. Salts

The word salt, like the word base, has been made somewhat ambiguous by developments of the last few years. In the most general sense *a salt is any product, other than solvent molecules, of the reaction of an acid with a base.* In most instances this product is an *ionic substance* or *ion pair*, such as sodium chloride, NaCl, which consists of the independent ions, Na^+ and Cl^-. A few salts, such as stannic chloride, $SnCl_4$, and aluminum chloride, Al_2Cl_6, are non-ionic or covalent salts—as proved by the fact that they readily melt or vaporize, and in the molten state are practically non-conductors of electricity (§ 142). *Inorganic salts* usually contain a metal (or the ammonium ion, NH_4^+), together with a non-metal or non-metallic group of atoms.

Soluble salts are generally prepared from the corresponding acids by the reactions of § 184, namely, by the reaction of acids with:

1. Metallic hydroxides.
2. Metallic oxides.
3. Sulfides.
4. Carbonates or sulfites; or, more generally, salts of *any volatile acid*, reacting with a non-volatile acid.
5. Many metals. (But this method is of little practical importance, since metals are expensive.)

Pause, now, for some equations to illustrate these five methods. (Ex. 19.)

Slightly soluble salts (often roughly described as *insoluble*) are usually prepared by the interaction of solutions of a soluble alkali or salt (to furnish the necessary cation) and a soluble acid or salt (to furnish the necessary anion):

$$\underset{\text{To furnish } Ba^{++}}{BaCl_2} + \underset{\text{To furnish } SO_4^{--}}{Na_2SO_4} \rightarrow BaSO_4\downarrow + 2NaCl$$

The arrow pointing downward directs attention to the formation of an insoluble substance, which separates as a *precipitate*. (Ex. 20.)

If the preceding equation is written

$$(Ba^{++} + 2Cl^-) + (2Na^+ + SO_4^{--})$$
$$\rightarrow (Ba^{++} + SO_4^{--})\downarrow + (2Na^+ + 2Cl^-)$$

we emphasize that each of the substances concerned in the reaction really consists of independent ions. There is no such thing as a molecule of the formula $BaCl_2$, Na_2SO_4, etc. *The ions do not combine with one another, even in forming the precipitate.* They are merely built into the space lattice of barium sulfate crystals, and exist there still, as independent ions. Since we cannot say that they "combine," let us merely say that they "produce" the precipitate.

If we write

$$Ba^{++} + SO_4^{--} \rightarrow BaSO_4\downarrow$$

we emphasize that any soluble barium salt and any soluble sulfate may be used for the production of barium sulfate. This generalized or ionic equation (§ 191) has the defect that it fails to remind us that such a reaction produces not only an *insoluble salt,* but also a *soluble acid or salt,* which may be recovered by evaporation or distillation, after filtering off the insoluble salt. (Ex. 21–26.)

The most important groups of insoluble salts are listed in a table in § 288.

Hydrolysis, § § 396–399, should be introduced at this place if needed to prepare for laboratory work involving it.

Technical Words

Acid—any substance capable of neutralizing a base. In a more restricted sense, any substance containing hydrogen which is capable of being transferred as protons, H^+, to another substance; in brief, a *proton donor.*

Strong or **weak**—conspicuously *active* or *slightly active.* These words should not be used to mean *concentrated* and *dilute,* except as modifiers of word *solution.*

Solvent—a substance used to dissolve another, to form a solution (§ 284).

Dissociate—to decompose, reversibly. **Proton,** p. 217.

Hydrogen ion—a general name for a proton, in combination with a molecule of solvent. Examples: H_3O^+, in a solution in water; NH_4^+, in liquid ammonia; $H_2C_2H_3O_2^+$, in glacial acetic acid.

Oxonium ion—the ion H_3O^+, formed by union of a proton with a molecule of water.

Chemical equilibrium, p. 65.

Ionize—to convert or be converted into ions, partially or completely, as by reaction with a solvent.

Ionization—the formation of ions, as by reaction with a solvent.

Degree of ionization, p. 221.

Conventional or **specialized equation**—an equation that employs conventional formulas (HCl, NaOH, NaCl, etc.) for reacting acids, bases, and salts, without regard to the fact that many of these are composed of separate, nearly independent ions, some of which are really not concerned in the given reaction.

Generalized or **ionic equation**—an equation that attempts to explain a reaction in terms of the ions (H^+, OH^-, Cl^-, etc.) actually concerned in it, neglecting other ions which may be added with the reacting ions, but which do not themselves react.

Base, p. 223. **Alkali** or **caustic alkali,** p. 224.

Hydrous oxide, p. 224. **Salt,** p. 225.

Ionic substance or **ion pair**—a substance composed of oppositely charged ions instead of electrically neutral molecules.

Precipitate—an insoluble solid formed in the midst of a liquid or gas as the result of a chemical reaction. It will ordinarily settle to the bottom or occasionally float to the top, owing to its having a different density from the surrounding medium.

Obsolete or Undesirable Terms

Monobasic, dibasic, tribasic. The modern terms are **monoprotic, diprotic, triprotic,** to refer to the number of hydrogen atoms in a molecule of an acid which may be transferred as protons to any proton acceptor.

Acid salts. It would be better to designate such salts as **acid anion salts,** to indicate that the acid properties reside in the anion; or as **hydrogen salts,** to indicate that they contain hydrogen, though they may or may not react acid toward indicators. Example: $NaHSO_4$, sodium hydrogen sulfate, which is sometimes called sodium acid sulfate, or even sodium bisulfate (a very undesirable term, now nearly obsolete).

Basic salt. For an **oxy-salt** or **hydroxy-salt,** such as Cu(OH)Cl(§ 399). Such salts do not often react alkaline.

Normal salt (for any salt not belonging to the two preceding groups).

Acid anhydride (except for a special group of organic compounds). Such a substance as sulfur dioxide is itself an acid, in the broadest sense of the word. It is best referred to as a **non-metallic oxide.**

Dissociation (when ionization is meant).

Hydronium ion and *hydroxonium ion* (for **oxonium ion**).

Summary

► § 184. Five different classes of substances that react with acids. The product, other than a salt, produced in each case.

Whether a salt can always be recovered by evaporating the solution in which the salt was produced.

► § 185. Simple tests for determining which of two acids is the more active. What must be true of equal volumes of the acid solutions, in making this comparison.

A few examples of acids differing in activity. What is meant by "strong" or "weak" acids.

► § 186. Whether the activity of a slightly active acid falls off proportionately, as the acid is diluted with water.

Evidence that the most active acids react with water in being dissolved in it or in being further diluted. Evidence that this reaction produces ions.

Evidence that hydrogen ions carry a positive and chloride ions a negative charge of electricity.

Two ways in which ions may conceivably be produced, when molecules of an active acid are dissolved in water.

Name given to the positively charged hydrogen atom. Name given to the ion produced when this particle combines with water.

Equations to show what is transferred when hydrogen chloride gas is dissolved in water or when it reacts with ammonia gas.

► § 187. Equation to show what happens when nitric acid is dissolved in water. Corresponding reaction between acetic acid and water.

What general conclusion may be drawn about the degree of completeness of the reaction of different sorts of acids with water.

How the degree of completeness may be indicated by the use of light and heavy arrows in writing an equation for a reversible reaction.

► § 188. What can be said with regard to the strength of the union between the proton and the rest of the acid molecule, in active acids. Similarly, for moderately active and slightly active acids.

► § 189. Equations to represent the two successive stages in the ionization of sulfuric acid. Names of the different ions produced in these reactions.

§ 190. Name given to the fractional part of the molecules of a substance which are converted into ions, under stated conditions. An example.

What happens to the degree of ionization of a slightly active acid, as the acid is more and more diluted with water. Why the term degree of ionization is somewhat indefinite.

► § 191. Equations to represent the five chief reactions of acids.

Advantage of generalized or ionic equations. When specialized equations must be used.

► § 192. The most common usage of the word base. Definition in terms of protons. A more general usage, recently adopted by some chemists.

Examples of some ions that would be recognized as bases because of their behavior toward protons.

A class of substances which some chemists would not regard as bases, though they do neutralize acids. What really happens when these substances react with acids. An equation to show what is transferred in reactions of this type.

Two classes of metallic hydroxides. Other names given to active and slightly active metallic hydroxides. Which of the light metal hydroxides is conspicuously different from the others, and in what respect.

§ 193. Five methods generally used for preparing soluble salts. An equation to illustrate each.

A general method for preparing insoluble salts. How we may indicate that the substances concerned in such a reaction really consist of independent ions and not of neutral molecules.

A name given to a slightly soluble substance, produced in the midst of a liquid or gas as the result of a chemical reaction.

Exercises

Write equations for the following reactions, *making sure that all formulas satisfy the requirements of valence* (§§ 168, 169).

1. Sodium hydroxide reacts with phosphoric acid.

2. Lead oxide reacts with acetic acid.

3. Sodium sulfide reacts with hydrobromic acid.

4. Calcium carbonate reacts with nitric acid.

5. Magnesium reacts with hydriodic acid.

6. Ammonium acetate reacts with sulfuric acid, yielding ammonium hydrogen sulfate, NH_4HSO_4, and acetic acid.

7. Ammonium hydrogen sulfate reacts with ammonium hydroxide, yielding ammonium sulfate and water.

8. Potassium hydrogen sulfate, reacting with potassium nitrate, yields potassium sulfate and nitric acid.

9. Write an equation showing the transfer of protons in a reaction between acetic acid and ammonia gas, forming the ions of ammonium acetate.

Check every formula in what follows to make sure that it satisfies the requirements of valence.

10. Write equations showing the transfer of protons when perchloric acid and hydrocyanic acid are dissolved in water. (These equations must indicate differences in the completeness of these reactions, due to differences in activity.)

11. Write equations showing the transfer of protons when ammonia gas reacts with nitric acid; also when it reacts in two successive steps with sulfuric acid.

12. Write equations to show the successive stages of ionization of oxalic acid and phosphoric acid. (Use light and heavy arrows to indicate whether each reaction is relatively complete or incomplete.)

13. Write an equation to show what is transferred when metallic aluminum reacts with an unspecified acid to form an aluminum salt.

14. Write an equation to show what is transferred when metallic tin reacts with an unspecified acid to form a stannous salt.

15. An unspecified hypochlorite (namely, hypochlorite ion) reacts with an unspecified acid to form hypochlorous acid. Represent by an ionic equation.

16. An unspecified nitrite (namely, nitrite ion) reacts with an unspecified acid to form nitric oxide (NO), nitrogen dioxide (NO_2), and water. Represent by an ionic equation.

17. Write equations to show how the two leading caustic alkalies may be prepared by treating the carbonate of the metal with calcium hydroxide, $Ca(OH)_2$, the other product being calcium carbonate.

18. Write an equation for the preparation of hydrous ferric oxide, $Fe(OH)_3$, by treating ferric chloride solution with a caustic alkali, the other product being a soluble chloride.

19. Write a conventional equation for the preparation of aluminum bromide, Al_2Br_6, by the reaction of hydrobromic acid with each of the substances suggested under the five headings of § 193.

20. Write a conventional equation for precipitation of silver chromate, Ag_2CrO_4, by the reaction of silver nitrate with sodium chromate.

21. Write and balance an equation for the formation of a precipitate of silver phosphate, Ag_3PO_4, together with sodium nitrate and nitric acid, by the reaction of silver nitrate with disodium phosphate, Na_2HPO_4.

Indicate the ions contained in each of the five substances appearing in the equation just written. Cancel out ions common to both sides of the equation and so obtain

an equation in which only the ions appear that are directly concerned with the formation of the precipitate.

22. Write a conventional equation for the formation of each of the following soluble salts from the corresponding carbonates, reacting with an acid: ammonium acetate, zinc bromide, calcium iodide, ferric nitrite, magnesium sulfate, manganese chloride, potassium oxalate.

23. Write equations showing how the salts just listed may be prepared from the hydroxides of the given metals.

24. Write equations for good methods for preparing the following insoluble salts, using an acetate in each instance to furnish the necessary cation and a sodium salt to furnish the necessary anion: silver chloride, mercurous iodide, calcium sulfate, barium chromate, mercurous sulfide, ferric hydroxide, cupric oxalate, calcium fluoride, ferrous phosphate.

25. Write an ionic equation for a reaction in which a hydrogen sulfate, (namely, hydrogen sulfate ion), reacting with a chloride, yields hydrogen chloride gas and a sulfate (namely, sulfate ion).

26. Write an ionic equation for the conversion of an unspecified carbonate into a hydrogen carbonate (namely, the hydrogen carbonate ion, HCO_3^-, by reaction with water and carbon dioxide.

It is important for the student to work all the preceding exercises. If he neglects to acquire reasonable skill in writing formulas and equations at this stage of his progress the ghost of his neglect will return to haunt him in most of the succeeding chapters.

To the Instructor

The facts of chemistry are of no intellectual significance and have but limited practical uses unless correlated and interpreted in the light of general theories. Yet the theories themselves are never properly understood unless viewed against a background of familiar facts.

So we have a contest of opinion. There are some who would unload a year's supply of chemical theory within the first few weeks of a course in chemistry, lest the chemical facts remain only facts and thus be nearly pointless; and others who would introduce a multitude of facts before attempting any theories, lest the theories remain nearly meaningless and of the substance of dreams.

This book attempts a middle course, by introducing at this point some ordinary facts, given in a very simple way, concerning chlorine, a typical nonmetal. In this way the student learns what we mean by the *chemical properties* of an element, and develops further skill in representing chemical reactions by *balanced equations*.

After that (Chapters 17–20), we attempt to explain why metals and nonmetals behave so differently, what takes place in forming molecules, and what is meant by oxidation and reduction, in a broadened sense. Then we revert to chlorine, treating it as a member of the halogen family of elements, reviewing the simple reactions previously made familiar, and explaining them in the light of what has been learned about the reasons why the atoms of different elements behave as they do.

Chapter 16

CHLORINE

► 194. Occurrence of Chlorine

Chlorine occurs in nature chiefly as sodium chloride, NaCl. This makes up 2.8 per cent of the ocean, which covers three fourths of the earth's surface to an average depth of about 3 miles. In addition, the ocean contains about 0.8 per cent of other dissolved salts, the most important being potassium chloride, KCl, and magnesium chloride, $MgCl_2$. Hydrogen chloride, HCl, is often plentiful in the gases belched forth by active volcanoes.

During past geological ages the evaporation of ocean water in shallow ponds, regularly flooded by the sea, led to the formation of immense deposits of salt, sometimes a thousand feet in thickness, in many different parts of the world. The lower layers of such strata are usually impure sodium chloride (rock-salt). The upper layers contain potassium chloride and frequently double salts, such as *carnallite*, $KCl \cdot MgCl_2 \cdot 6H_2O$.

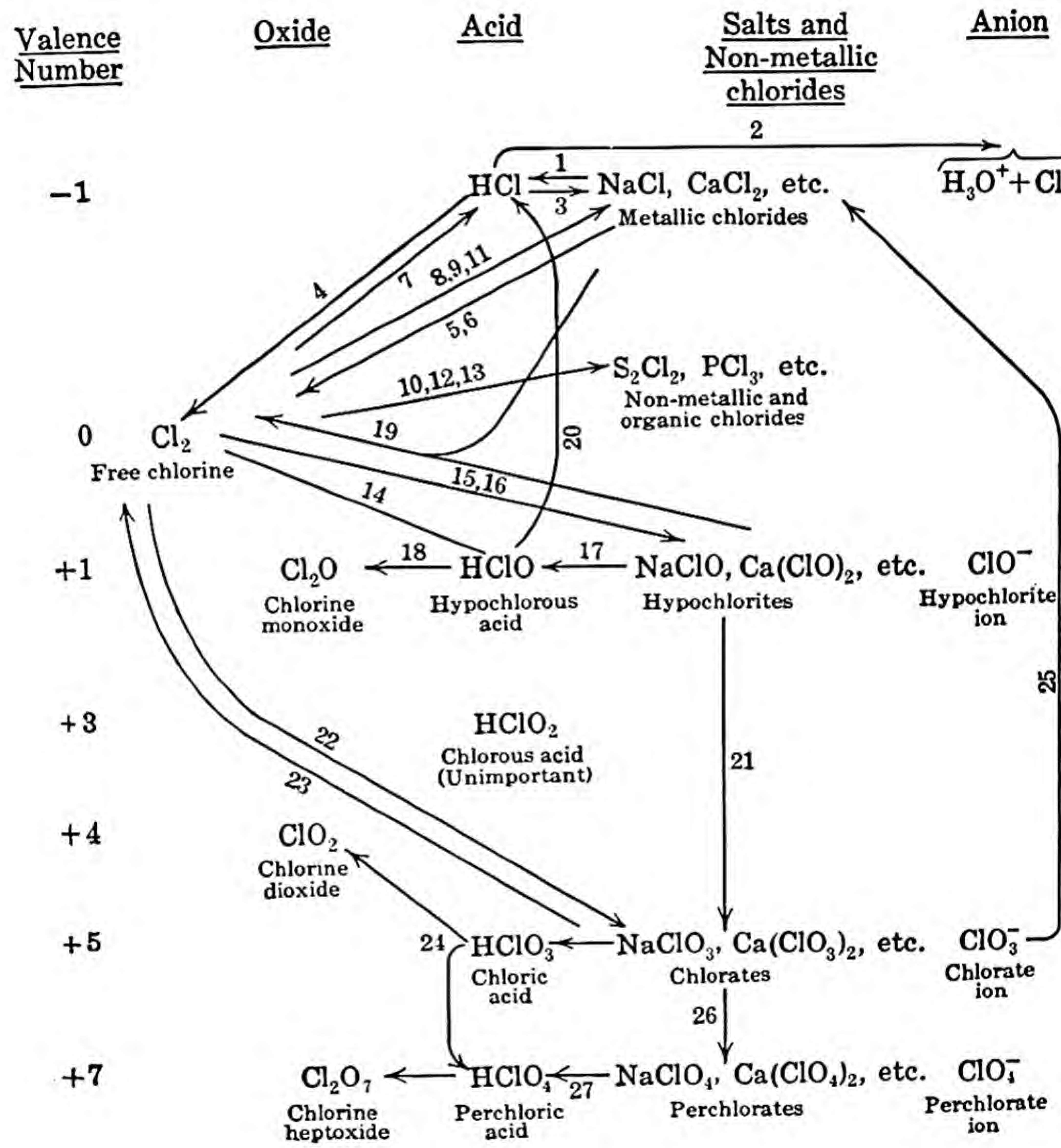
► 195. The Valence States of Chlorine

In this book an element is often introduced by a table showing its chief compounds, in connection with the valence number (§ 171) that the element displays in each compound.

Each horizontal line in this table (next page) represents the same *valence number*, *valence state*, or *stage of oxidation* of the element, on an arbitrary basis (not always justified) which assumes for each oxygen atom (except in peroxides) an electrical charge of -2 and for each hydrogen atom (except in metallic hydrides) a charge of $+1$.

Thus in chlorine monoxide, Cl_2O, if we give the oxygen atom a charge of -2, then each chlorine atom must possess a charge of $+1$ (the *valence number* of chlorine in Cl_2O) in order that the molecule as a whole may be electrically neutral. In hypochlorite ion, ClO^-, the ion as a whole (not merely the oxygen atom) carries a charge of -1; hence if we give the oxygen atom a charge of -2, that of the chlorine

atom must be +1 (the valence number of chlorine in ClO^-). The student should pause now, to prove to his own satisfaction that every formula in this table really represents chlorine in the valence number that is assigned to it. (Ex. 1–3.)



Every chapter that is headed with a table of this sort should be begun by memorizing the valence states of the element, and the names and formulas that represent each. Then note how many numbered arrows there are. These represent the chief reactions of the element and its compounds. Then as you work through the chapter you will find that the important equations are numbered to correspond with the numbered arrows (unimportant equations being left unnumbered).

With chlorine, in the present chapter, there are just 27 important equations, not an unlimited number. When these have been mastered and a few variations worked out (as presented in exercises at the end of the chapter), you will be acquainted with the chemical properties of chlorine.

► 196. Hydrogen Chloride and Hydrochloric Acid

In an earlier chapter (§ 165) we learned that volatile acids, including hydrogen chloride gas, are produced by heating their salts with a non-volatile acid (commonly sulfuric acid or phosphoric acid):

Equation 1: $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \uparrow$

Hydrogen chloride is a colorless gas with a sharp odor. When exposed .o moist air it reacts with the water vapor in the air to produce hydrochloric acid. Moisture then condenses about the acid ions to form a multitude of microscopic liquid droplets of hydrochloric acid, visible to the eye as a faint cloud.

In the reaction of hydrogen chloride with water, previously discussed (§ 186), the water serves as a base in accepting protons from the hydrogen chloride gas:

Equation 2: $$\underbrace{HCl \quad + \quad H_2O}_{H^+ \text{ (transferred)}} \rightarrow \underbrace{\underset{\text{Oxonium-ion}}{H_3O^+} \quad + \quad \underset{\text{Chloride-ion}}{Cl^-}}_{\text{Hydrochloric acid}}$$

We usually represent hydrochloric acid itself by the formula HCl, which properly belongs to the gas hydrogen chloride. It is a typical *active acid*, reacting with metals, metallic oxides, alkalies, carbonates, sulfites, and sulfides as described in §§ 184, 191. In all these reactions one of the products is a *salt* (a chloride):

Equations 3: $$\left.\begin{array}{l} Na,\ Na_2O,\ NaOH \\ Na_2CO_3,\ Na_2SO_3 \text{ or } Na_2S \end{array}\right\} + HCl \rightarrow NaCl + ?$$
(Ex. 4.)

The student should pause to decide what product other than the metallic chloride is obtained in each case. Then rewrite the six equations in ionic form, representing hydrochloric acid by H^+, the conventional symbol for an acid. (Ex. 4.)

The reaction of hydrogen chloride with ammonia gas (§ 186) is like its reaction with water, except that NH_4^+ is formed instead of H_3O^+. Notice the heavy white fumes, really clouds of minute crystals of ammonium chloride, that are formed whenever the stoppers of bottles

containing hydrochloric acid and ammonium hydroxide are brought together. Moisture serves as a catalyst in this reaction; hydrogen chloride and ammonia fail to react if both gases have been very carefully dried. (Ex. 5.)

Hydrochloric acid is the chief laboratory source of chlorine. It is occasionally used in industry in cleaning metals, in removing mineral matter from bones, previous to extraction of glue, and in converting cornstarch into glucose.

► 197. Preparation of Chlorine in the Laboratory

Chlorine may be prepared in the laboratory by oxidizing hydrochloric acid with manganese dioxide:

Equation 4: $$4HCl + MnO_2 \rightarrow \underset{\text{Manganese tetrachloride}}{MnCl_4} + 2H_2O$$
$$\hookrightarrow MnCl_2 + Cl_2\uparrow$$

If the mixture is kept cool, manganese tetrachloride is produced. This decomposes on being heated, and chlorine gas is set free.

Concentrated hydrochloric acid contains 60 per cent water, hence inconvenient quantities of water are distilled off with the chlorine, if one prepares chlorine as just described. It is better to use a mixture of solid common salt and manganese dioxide, to which concentrated sulfuric acid is added. (This contains very little water.) When we heat the mixture (Fig. 81) the acid reacts with the salt to produce hydrogen chloride gas, which is then oxidized by the manganese dioxide. The final result, when an excess of sulfuric acid is employed, is expressed by

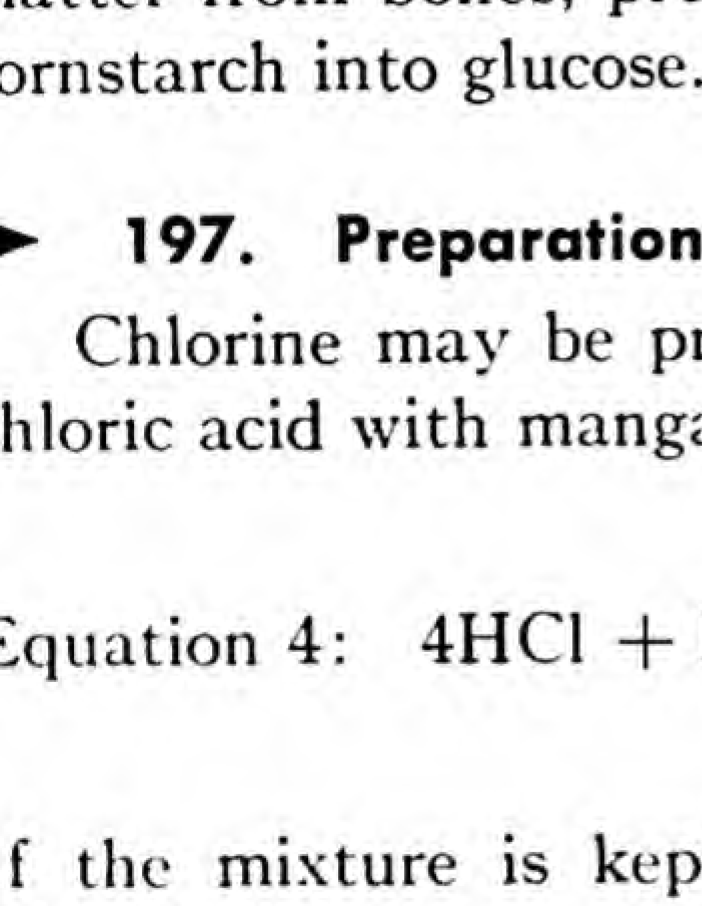


FIG. 81. Laboratory preparation of chlorine. The tube *A* is filled with alternate layers of charcoal and soda lime to prevent escape of chlorine into the atmosphere.

Equation 5:

$$2NaCl + 3H_2SO_4 + MnO_2 \rightarrow$$
$$2NaHSO_4 + MnSO_4 + Cl_2\uparrow + 2H_2O$$

Observe that all the chlorine in the original chloride is here set free as elementary chlorine, instead of only half of it, as in the preceding reaction.

Actually, a great many other *oxidizing agents* might be used instead of the manganese dioxide. Any one of them will oxidize the hydrogen

chloride to water and chlorine and be itself reduced. Details will be given when we are better prepared to discuss what actually takes place (§ 244).

► 198. Preparation of Chlorine by Electrolysis

When an electric current is passed through a purified solution of common salt (Fig. 82) hydrogen gas is liberated at the *cathode* (negatively charged electrode), and chlorine gas at the *anode* (positively charged electrode). The reaction may be most simply represented:

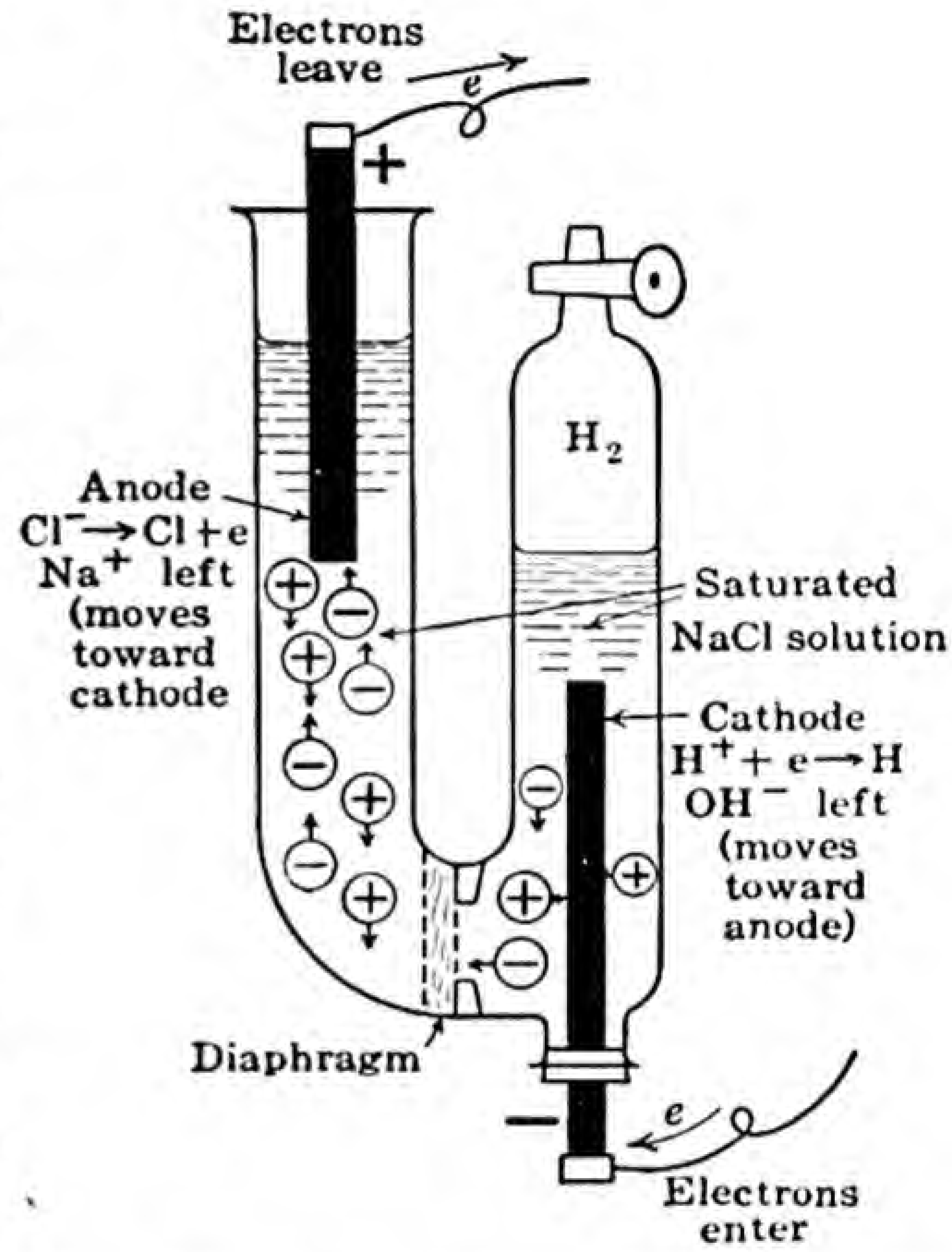


FIG. 82. Preparation of chlorine by electrolysis (lecture demonstration).

Equation 6:

$$2NaCl + 2H_2O + \text{electrical energy} \rightarrow H_2\uparrow + Cl_2\uparrow + 2NaOH$$

But consider the *ions* concerned. Protons (supplied by the water) accept electrons from the cathode (negatively charged electrode) and become hydrogen atoms, which combine in pairs to form molecules:

Equation 6(*a*):

$$2H^+ + \underset{\text{From cathode}}{2e} \rightarrow 2H \;\; \hookrightarrow \underset{\text{Set free at cathode}}{H_2\uparrow}$$

OH^- ions, left in solution, migrate toward anode.

Chloride ions (supplied by the salt) yield electrons to the anode (positively charged electrode) and become chlorine atoms, which combine in pairs to form chlorine molecules.

Equation 6(*b*):

$$2Cl^- \rightarrow 2Cl \;\; \hookrightarrow \underset{\text{Set free at anode}}{Cl_2} + \underset{\text{Delivered to anode}}{2e}$$

Na^+ ions, left in solution, migrate toward cathode.

If we ask why certain ions are discharged at the electrodes and others are left behind in the solution, the answer is that at each electrode the reaction takes place which demands the least *energy*.

Figure 83 shows the cross section of a commercial cell for the production of chlorine by electrolysis. *The asbestos diaphragm separating anode and cathode is to prevent the chlorine gas that is liberated at the anode from reacting with the sodium hydroxide produced at the cathode.* If it did, the result would be a hypochlorite (§ 204).

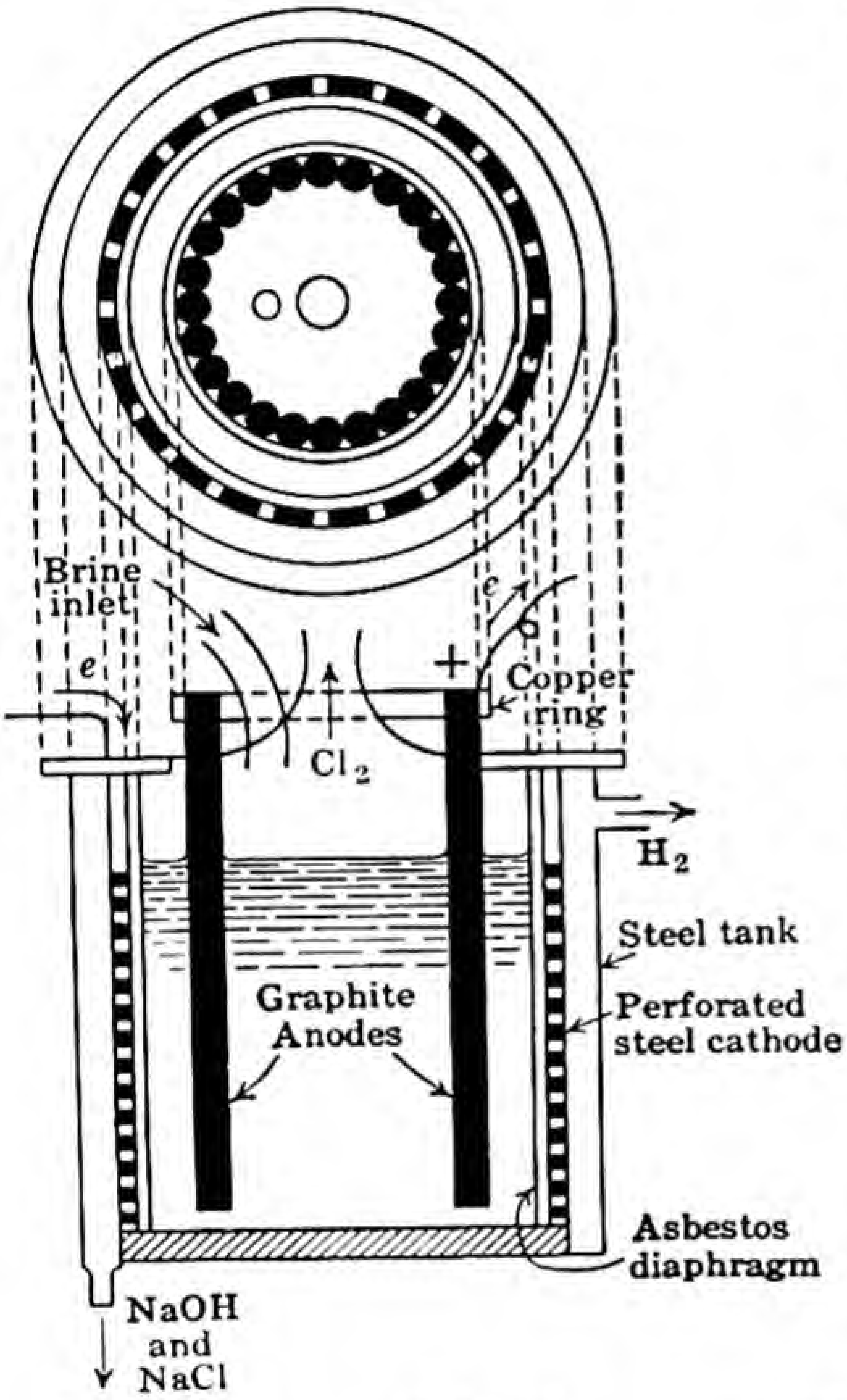


FIG. 83. Vorce cell for the commercial production of chlorine by electrolysis. Purified brine is admitted at the top of the cell.

On evaporating the electrolyzed solution any *unchanged sodium chloride* that still remains soon crystallizes out and may be removed; then further evaporation yields solid *sodium hydroxide*, NaOH. The chlorine obtained in the process is usually liquefied and marketed in cylinders or tank cars. The hydrogen may be burned as fuel or combined with chlorine to form hydrogen chloride.

► 199. Physical Properties of Chlorine

Chlorine is a greenish yellow gas, easily liquefied. It has a powerful irritating odor. Relief from discomfort caused by inhaling traces of chlorine is obtained by breathing through a handkerchief wet with alcohol or acetone. Chlorine has about $2\frac{1}{2}$ times the density of air. (Ex. 6.)

Chlorine is fairly soluble in water (about 2 volumes of the gas in 1 of water at room temperature). If the solution in water is cooled *chlorine hydrate*, $Cl_2 \cdot 8H_2O$, separates as greenish yellow crystals.

► 200. Direct Union of Chlorine with Other Elements

Chlorine combines directly with most other elements (the principal exceptions being carbon, nitrogen, oxygen, fluorine, and the inert gases):

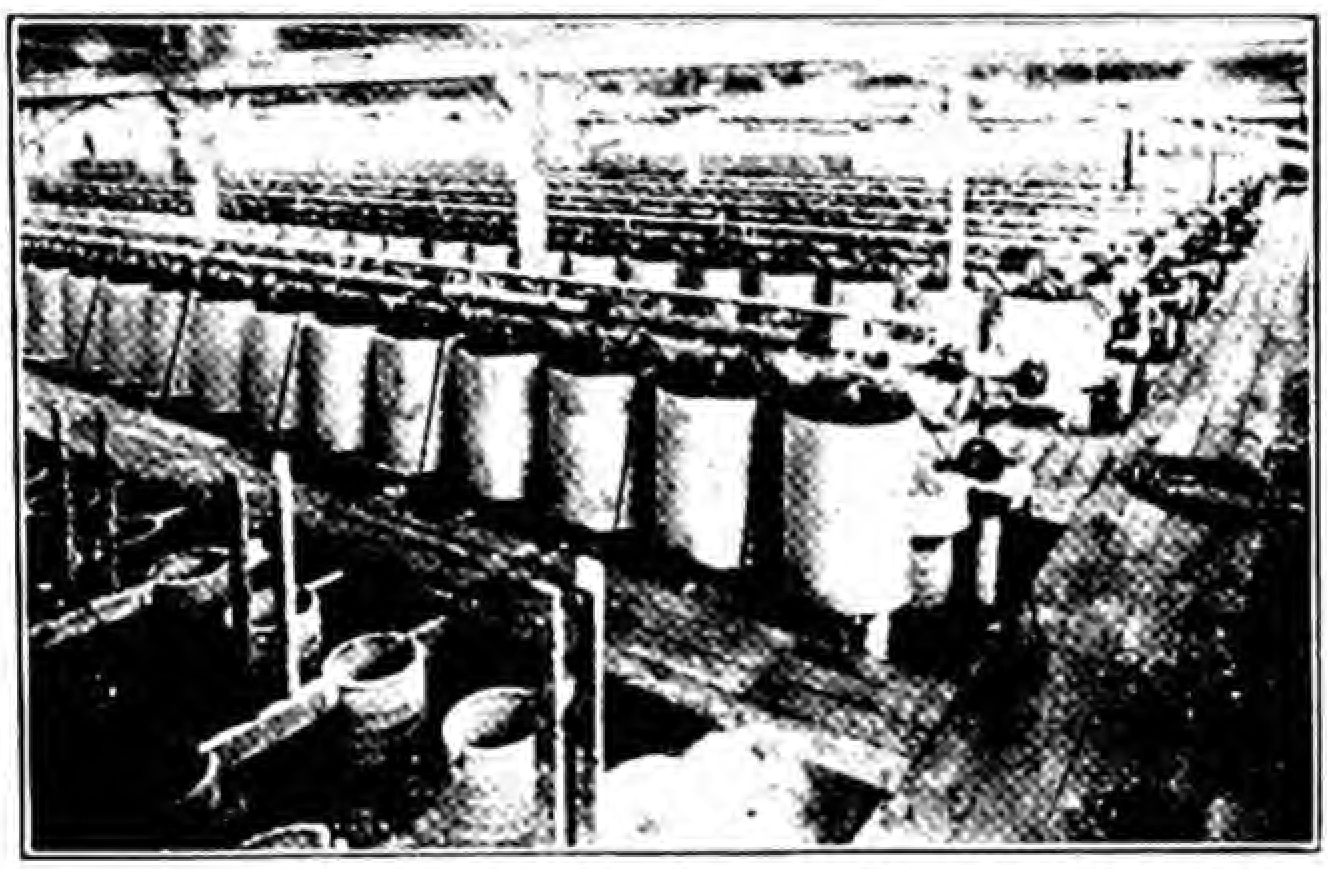
1. With *hydrogen*, chlorine combines very slowly in dull light, and explosively when exposed to direct sunlight or the light of a burning magnesium ribbon (explanation in § 335):

Equation 7: $$H_2 + Cl_2 \rightarrow 2HCl$$

A trace of water vapor must be present to serve as a catalyst in this reaction.

Instead of mixing the hydrogen and chlorine and exploding the mixture we may intermingle and burn the two gases in a burner of acid-proof material. They then combine quietly, with a pale flame, producing dense fumes of hydrogen chloride, which may be dissolved in water to form hydrochloric acid (occasionally prepared commercially by this method).

2. Most of the *metals* burn brilliantly in an atmosphere of chlorine. Examples: sodium, potassium, magnesium, aluminum, zinc, iron,



Courtesy of the Westvaco Chemical Products Co.

FIG. 84. Commercial production of chlorine by electrolysis.

copper, mercury. The student should write equations for these reactions, the product obtained with the three metals last named being the lower-valence (*-ous*) or the higher-valence (*-ic*) salt (§ 169) according as a limited amount of chlorine is used, or an excess of chlorine. (Ex. 7.)

Antimony catches fire in chlorine spontaneously.

Equation 8: $$2Sb + \underset{\text{(Limited amount)}}{3Cl_2} \rightarrow 2SbCl_3$$

The vapors of the product, antimony trichloride, are poisonous and should not be breathed. An excess of chlorine would yield antimony pentachloride, $SbCl_5$.

3. Metallic oxides do not react with chlorine, unless strongly heated with carbon, while a current of chlorine is passed over them. Oxides of heavy metals then often react, being vaporized as heavy-metal chloride. The oxygen of the heavy-metal oxide takes its depar-

ture as carbon monoxide. This is an important method for preparing certain metallic chlorides in the *anhydrous* condition:

Equation 9: $Al_2O_3 + 3C + 3Cl_2 \rightarrow \underset{\text{(Vaporized)}}{Al_2Cl_6\uparrow} + 3CO\uparrow$

4. Sulfur, phosphorus, and a number of other *non-metals* (but not carbon) combine with chlorine to form *volatile chlorides*, when they are heated in a current of chlorine gas:

Equations 10: $2S + \underset{\text{(Limited amount)}}{Cl_2} \rightarrow \underset{\text{Sulfur monochloride}}{S_2Cl_2\uparrow}$ $\quad S + \underset{\text{(Plentiful supply)}}{2Cl_2} \rightarrow \underset{\text{Sulfur tetrachloride}}{SCl_4}$

$$P + \underset{\text{(Limited amount)}}{1\tfrac{1}{2}Cl_2} \rightarrow \underset{\text{Phosphorus trichloride}}{PCl_3} \qquad P + \underset{\text{(Plentiful supply)}}{2\tfrac{1}{2}Cl_2} \rightarrow \underset{\text{Phosphorus pentachloride}}{PCl_5}$$

We may double each of the two equations last given, to clear of fractions. Here again we see that *the formula of the product obtained in a chemical reaction often depends on the proportions in which the reactants are brought together.*

Chlorine combines with bromine and iodine to form BrCl, ICl, and ICl_3, which have chemical properties not very different from those of the elements that compose them.

The valence number of chlorine in non-metallic chlorides may be taken as -1, in lack of conventions regarding the valence number of the other element. The difficulty is that the two elements in such compounds do not really carry separate charges (+ or −) but jointly *share electrons* (as discussed, hereafter, in § 243). (Ex. 8, 9.)

► 201. Reaction of Chlorine with Bromides and Iodides

Chlorine reacts with bromides and iodides to set free elementary bromine and iodine:

Equations 11: $Cl_2 + 2NaBr \rightarrow 2NaCl + Br_2$

$$Cl_2 + 2NaI \rightarrow 2NaCl + I_2$$

The chlorine here appears to *displace* bromine or iodine from the bromide or iodide.

Similar equations would represent the action of chlorine on bromides and iodides, whatever the valence of the metal:

$$Cl_2 + CaBr_2 \rightarrow CaCl_2 + Br_2$$

$$3Cl_2 + Al_2Br_6 \rightarrow Al_2Cl_6 + 3Br_2$$

These reactions are the means for preparing elementary bromine and iodine from bromides and iodides, and for testing for the presence of bromides and iodides in mixtures (§ 282). Be sure never to add any very great excess of chlorine, else this, in the presence of water (yielding oxygen), will oxidize the free iodine to iodic acid.

► 202. The Reaction of Chlorine with Hydrocarbons

Thousands of organic compounds contain chlorine. Dozens of these are of great industrial importance. Very frequently we make these compounds by treating a hydrocarbon with chlorine, or by a series of reactions in which *chlorination* plays a part. Ordinarily, the chlorine reacts with a hydrocarbon either by *direct addition*, as in

Equation 12: $$\underset{\text{Ethylene gas}}{C_2H_4} + Cl_2 \rightarrow \underset{\text{Ethylene dichloride (liquid)}}{C_2H_4Cl_2}$$

or, in many instances, chlorine enters the molecule by an *exchange*, as in

Equation 13: $$\underset{\text{Methane gas}}{CH_4} + Cl_2 \rightarrow \underset{\text{Methyl chloride (volatile liquid)}}{CH_3Cl} + HCl$$

An exchange reaction in which an organic compound has one element partially or completely replaced by another is called *substitution*. (Ex. 10.)

Though most hydrocarbons react with chlorine either by direct addition or by substitution, turpentine (chiefly *pinene*) catches fire in chlorine, emitting gusts of acid fumes mixed with black smoke (finely divided carbon):

$$\underset{\text{Pinene}}{C_{10}H_{16}} + 8Cl_2 \rightarrow 16HCl + 10C$$

► 203. The Reaction of Chlorine with Water

A dilute solution of chlorine gas in water first turns litmus red, then bleaches it. The reddening is due to hydrochloric acid (active acid), and the bleaching to hypochlorous acid (slightly active acid, but vigorous bleaching agent). So we have evidence that chlorine, on being dissolved in water, reacts with the water:

Equation 14: $$H_2O + Cl_2 \underset{(b)}{\overset{(a)}{\rightleftharpoons}} HCl + \underset{\text{Hypochlorous acid}}{HClO}$$

Since the solution thus obtained is greenish it doubtless contains some unchanged chlorine. In other words, the reaction from left to right remains incomplete. So once more (as in §§ 90, 187) we account for the incompleteness of a reaction by its being reversible. *Equilibrium in a saturated solution of chlorine in water occurs when about one third of the chlorine has been converted into hypochlorous acid and hydrochloric acid.*

Moist chlorine bleaches many colored dyestuffs (but not printer's ink, which is really a suspension of finely divided carbon). *Bleaching by chlorine requires the presence of moisture, and is really due to the hypochlorous acid that is formed whenever chlorine reacts with water.*

► 204. Preparation of Hypochlorites

We have just seen that the interaction of chlorine with water is reversible. If by any means we interrupt the right-to-left reaction (*b*), the left-to-right reaction (*a*) will keep on going until it becomes complete. The obvious way is to add an alkali or a soluble carbonate, thus so greatly decreasing the concentration of the acids (HCl and HClO) demanded by (*b*) that (*b*) practically ceases. Then instead of the acids we obtain their salts (NaCl and NaClO). In brief, *chlorine reacts completely with solutions of alkalies and soluble carbonates to form a mixture of hypochlorite and chloride:*

Equation 15: $$2NaOH + Cl_2 \rightarrow NaCl + \underset{\text{Sodium hypochlorite}}{NaClO} + H_2O$$

Equation 16: $$Na_2CO_3 + Cl_2 \rightarrow NaCl + NaClO + CO_2 \uparrow$$

The solution must be kept cold, else the hypochlorite is converted into chlorate (§ 206).

A solution of sodium chloride and sodium hypochlorite, prepared from sodium carbonate as just indicated, with some boric acid added, has been used in surgery for the disinfection of wounds, which were sometimes irrigated with the solution during weeks or months. More recent practice (the Orr method) is content to cleanse the wound, cut away dead tissue, then immobilize the area in a plaster cast.

Commercially, hypochlorites are often made by electrolysis of a solution of common salt, keeping the solution cold, and stirring it to bring the chlorine and sodium hydroxide that are produced into contact, instead of keeping them separated by an asbestos diaphragm (§ 198).

If calcium hydroxide (slaked lime) is treated with chlorine the result is *bleaching powder* (sometimes still called "chloride of lime").

This is shown by X-ray examination to consist of crystals of *hydroxy-hypochlorite*, $Ca(ClO)_2 \cdot 2Ca(OH)_2$, intermingled with crystals of *hydroxy-chloride*, $CaCl_2 \cdot Ca(OH)_2 \cdot H_2O$. Pure calcium hypochlorite, $Ca(ClO)_2 \cdot 2H_2O$, and the corresponding anhydrous salt are often sold under the name "high-test hypochlorite" (H.T.H.). They are stable substances when kept dry.

Solid bleaching powder is used as a disinfectant and deodorizer because the calcium hypochlorite in it slowly reacts with carbon dioxide and moisture of the air, to liberate hypochlorous acid, which is a powerful oxidizing agent. The odor of bleaching powder is probably chiefly that of chlorine monoxide, derived from the hypochlorous acid as explained below.

205. Reactions of Hypochlorites

The chief reactions of the hypochlorites may be summarized under five headings:

1. *Hypochlorites and bleaching powder are not themselves bleaching agents;* but *dilute solutions*, on being *faintly acidified*, liberate hypochlorous acid, which does bleach effectively:

Equation 17: $NaClO + H_2SO_4 \rightarrow NaHSO_4 + \underset{\text{(Bleaching agent)}}{HClO}$

When hypochlorous acid serves as a bleaching agent it is reduced to hydrochloric acid. (Ex. 11.)

2. If a strong solution of a hypochlorite (*in absence of chloride*) is acidified, the hypochlorous acid set free decomposes to a large extent, liberating *chlorine monoxide*, Cl_2O, a yellowish, violently explosive gas with a pungent odor, much like that of chlorine itself:

Equation 18: $2HClO \rightarrow Cl_2O + H_2O$

3. *If both hypochlorite and chloride are present in a solution the addition of a slightly active acid or of very dilute sulfuric acid liberates hypochlorous acid; but a more active or more concentrated acid liberates chlorine:*

Equation 19:

$$NaCl + NaClO + 2H_2SO_4 \rightarrow \underbrace{HCl + HClO}_{\rightarrow H_2O + Cl_2} + 2NaHSO_4$$

4. In the presence of a trace of cobalt salt, to serve as a catalyst, the preceding reaction liberates oxygen, instead of chlorine:

Equation 20: $HClO \rightarrow HCl + \frac{1}{2}O_2$

The same reaction takes place when a solution of chlorine in water (which always contains hypochlorous acid, § 203) is exposed to sunlight. Here we see that a catalyst may not merely hasten a reaction but may completely alter its character, by favoring a different reaction, which in the absence of the catalyst may have remained imperceptible.

5. Conversion of a hypochlorite into a chlorate, as next described.

206. Chlorates and Chloric Acid

When a solution of a hypochlorite is heated the product is a mixture of chloride and chlorate:

Equation 21: $$3NaClO \rightarrow 2NaCl + NaClO_3$$

Observe that every third hypochlorite ion takes the oxygen from two others.

If chlorine is passed into a *hot* solution of an alkali, a mixture of chloride and chlorate is obtained directly:

Equation 22: $$6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

Commercially, by electrolysis of a hot solution of calcium chloride, vigorously stirred, one may produce calcium chlorate. This is then converted into a slightly soluble salt, potassium chlorate, by an exchange reaction with potassium chloride. (Ex. 12.)

Chlorates, in dilute acid solution, are moderately vigorous oxidizing agents, in other words, are reduced to chlorides by most reducing agents.

Dry chlorates are dangerously vigorous oxidizing agents. One should never mix them, dry, with oxidizable material, except in the presence of a large excess of some inert substance, such as sodium carbonate, to moderate the violence of the reaction. *The mere grinding of a chlorate with oxidizable material has often resulted in a violent and fatal explosion.*

Chlorates, in presence of dilute acids, will oxidize chlorides, liberating chlorine:

Equation 23: $$KClO_3 + 5KCl + \underset{\text{(Dilute!)}}{6H_2SO_4} \rightarrow 6KHSO_4 + 3Cl_2 + 3H_2O$$

Concentrated acids should never be added to dry chlorates. The result is chloric acid, $HClO_3$, which decomposes into chlorine dioxide (along with perchloric acid and water):

Equation 24. $$3HClO_3 \rightarrow HClO_4 + \underset{\text{(Explodes)}}{2ClO_2} \uparrow + H_2O$$

The chlorine dioxide *explodes violently*, yielding chlorine and oxygen.

Chlorates are so dangerous that unauthorized and unsupervised experiments with them should never be performed. They are used in industry as oxidizing agents in the manufacture of *matches*, *fireworks*, *percussion caps* for small arms ammunition, and a few explosives. Chlorate solutions are effective *weed killers*, but one should bear in mind the serious fire hazard produced if such solutions are spilled on floors or clothing and permitted to evaporate. A chance spark or a little friction invites disaster.

207. Perchlorates and Perchloric Acid

When a chlorate is strongly heated, or melted in the presence of a catalyst (§ 45, item 1), it yields oxygen and is converted into a chloride:

Equation 25: $$2KClO_3 \xrightarrow{\text{Catalyst}} 2KCl + 3O_2$$

More cautiously heated, just above its melting point, in the absence of a catalyst, a chlorate is converted into a mixture of perchlorate and chloride:

Equation 26: $$4KClO_3 \rightarrow 3KClO_4 + KCl$$

Ordinarily some oxygen gas escapes at the same time. With care, not more than a fifth of the oxygen in the chlorate is thus lost before the rest of the salt has been converted into perchlorate.

Perchlorates are produced commercially by the electrolysis of a cold solution of sodium chlorate. To the perchlorate solution thus obtained potassium or ammonium chloride is added, to precipitate potassium or ammonium perchlorate (which are but slightly soluble). Perchlorates in general are extremely soluble.

A perchlorate may be distinguished from a chlorate by the addition of a drop of *dilute* hydrochloric acid to a single crystal of the salt. The perchlorate gives perchloric acid (colorless), whereas the chlorate gives chloric acid, which decomposes with the liberation of chlorine dioxide, ClO_2. This colors the solution yellow.

Perchloric acid, $HClO_4$, may be made by adding *dilute* sulfuric acid to a solution of barium perchlorate:

Equation 27: $$Ba(ClO_4)_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2HClO_4$$

The solution is then filtered to remove barium sulfate, and concentrated by removing water by distillation *at a low temperature under reduced pressure* (§ 153). When the liquid has been concentrated to contain not to exceed 70 per cent perchloric acid the distillation is interrupted, since the pure acid is dangerously explosive.

Perchloric acid is prepared commercially by oxidizing ammonium perchlorate, by boiling a solution of this salt with aqua regia (§ 88), then concentrating the solution under diminished pressure, as just described:

$$34NH_4ClO_4 + 8HCl + 36HNO_3 \rightarrow$$
$$34HClO_4 + 35N_2O\uparrow + 4Cl_2\uparrow + 73H_2O$$

► Although perchloric acid is a vigorous oxidizing agent it is far less dangerous than chloric acid. *By diluting a solution of perchloric acid its oxidizing properties may be weakened as desired.* In very dilute solutions it is a typical active acid, with practically no tendency to serve as an oxidizing agent.

By treating perchloric acid with a vigorous dehydrating agent, such as phosphorous pentoxide, P_2O_5, then distilling in a vacuum, a volatile oily liquid, the dangerously explosive *chlorine heptoxide,* or *perchloric acid anhydride,* Cl_2O_7, is obtained:

$$2HClO_4 + P_2O_5 \rightarrow Cl_2O_7\uparrow + 2HPO_3$$

► 208. Uses of Chlorine

The United States, in an average year, uses more than 200,000 tons of liquid chlorine. About 80 per cent of this is used in *bleaching paper pulp, paper,* and *cotton* and *linen textiles.* (Chlorine injures silk and wool.) Very often solutions of chlorine itself are employed; at other times the chlorine is converted into a hypochlorite or bleaching powder, which on being acidified, in a *dilute solution,* releases hypochlorous acid, to accomplish the bleaching.

The *water supplies* of large cities are nearly always treated with very small amounts of chlorine for the destruction of bacteria responsible for typhoid and occasionally other epidemic diseases The chlorine (a few tenths of a part per million parts of water) is added to the water after preliminary filtration to remove suspended matter. Subsequently the water may be sprayed into the air to aerate it sufficiently to improve its taste and odor. In *superchlorination* the water is treated with as much as two or three parts of chlorine per million, as an extra precaution against accidental pollution. The surplus chlorine may then be removed by filtration through activated charcoal.

Chlorine is also used in the preparation of *anhydrous* metallic chlorides and many important organic compounds containing chlorine (§ 202).

► 209. Volumes of Reacting Gases

Review § 116.

The reactions of this chapter afford a good opportunity to consider problems in which we wish to know what *volume* of a gas is concerned in a given reaction. Consider, for example, the direct union of hydrogen and chlorine to produce hydrogen chloride:

$$H_2 + Cl_2 \rightarrow 2HCl$$

Observe that one molecule of hydrogen is needed for one molecule of chlorine, to produce two molecules of hydrogen chloride. Now equal numbers of molecules occupy equal volumes (Avogadro's principle, § 31). We conclude that our reaction demands *equal volumes* of hydrogen and chlorine gas and produces twice that volume of hydrogen chloride gas. If 10 ml of hydrogen gas and 12 ml of chlorine gas are intermingled and exploded, there will be left an excess of 2 ml of chlorine, and the volume of hydrogen chloride produced will be twice that of the hydrogen or chlorine used, *i.e.*, will be 20 ml. (Ex. 13.)

Be sure to apply this method only to substances that are actually gases or vapors under the conditions of the experiment. For example, in the reaction

$$\underset{\text{(Solid)}}{Al_2O_3} + 3Cl_2 + \underset{\text{(Solid)}}{3C} \xrightarrow{\text{Heated}} \underset{\text{(Vaporized)}}{Al_2Cl_6} + 3CO$$

the aluminum oxide and carbon are *solids* (of negligible volume in comparison with the gases concerned in the reaction). The reaction uses three molecules of gaseous chlorine to produce three molecules of gaseous carbon monoxide. We conclude that the volume of chlorine used is equal to the volume of carbon monoxide produced.

Aluminum chloride vaporizes as molecules of the formula Al_2Cl_6. We see that one such molecule is produced for every three molecules of chlorine employed; hence 3 volumes of chlorine gas will be needed for each volume of aluminum chloride vapor, at any given temperature. The student will gradually learn which of the substances he encounters are really gases or vapors under the condition of the experiment, and which are solids and liquids and therefore of nearly negligible volume. (Ex. 14.)

We often encounter problems involving a *volume* of a gas and a *weight* of some other substance. For example, *what volume of chlorine will react with 10 grams of sodium hydroxide*, in the reaction

$$Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$$

Over the formulas appearing in the equation we write the *actual* weights and volumes mentioned in the problem. Beneath the formulas we write the quantities *indicated* by the number of moles represented by the equation:

$$\begin{array}{lccccccccc}
\textit{Actual:} & x\ \textit{liters} & & 10\ \textit{grams} & & & & & & \\
 & Cl_2 & + & 2NaOH & \rightarrow & NaCl & + & NaClO & + & H_2O \\
\textit{Indicated:} & \begin{array}{c}1\text{ mole}\\ = 22.4\ \textit{liters}\end{array} & & \begin{array}{c}2\text{ moles}\\ = 2 \times 40\\ = 80\ \textit{grams}\end{array} & & & & & &
\end{array}$$

Since the problem calls for a *volume* of chlorine we express this as *x liters;* then the 1 mole of chlorine appearing in the equation must be expressed in the same unit, and will represent 22.4 *liters*, under standard conditions (§ 116). (Observe that the formula Cl_2 represents 2 gram atoms of chlorine, but only 1 mole.) But the actual quantity of sodium hydroxide mentioned in the problem is 10 *grams*. Then the 2 moles of sodium hydroxide appearing in the equation must be expressed in the same unit; it will be 80 *grams*.

Now we observe that the *actual* quantity of sodium hydroxide is 10/80 of the *indicated* quantity. The actual quantity of chlorine will therefore be this same fraction of the indicated quantity; that is,

$$\frac{10}{80} \times 22.4 = 2.8\ \textit{liters}$$

In the reaction

$$4HCl + MnO_2 \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

we notice that we have four molecules of hydrogen chloride gas for every molecule (Cl_2) of chlorine gas. Therefore 4 *volumes* of hydrogen chloride will be needed for every volume of chlorine produced. Now let us ask *what weight of manganese dioxide is needed for each liter of chlorine gas produced (under standard conditions).*

$$\begin{array}{lccccccccc}
\textit{Actual:} & & & x\ \textit{grams} & & & & 1\ \textit{liter} & & \\
 & 4HCl & + & MnO_2 & \rightarrow & MnCl_2 & + & Cl_2 & + & 2H_2O \\
\textit{Indicated:} & & & \begin{array}{c}1\text{ mole}\\ = 87\ \textit{grams}\end{array} & & & & \begin{array}{c}1\text{ mole}\\ = 22.4\ \textit{liters}\end{array} & &
\end{array}$$

Since the actual quantity of chlorine mentioned in the problem is 1 *liter* the indicated quantity must be in the same unit. It is 1 mole = 22.4 *liters* (under standard conditions). But the actual quantity of manganese dioxide is in *grams*, hence the indicated quantity must also be in grams. It is 1 mole = 87 grams.

Now the actual quantity of chlorine is 1/22.4 of the indicated quantity. The actual quantity of manganese dioxide will therefore be this same fraction of the indicated quantity; that is, $1/22.4 \times 87 =$ 3.88 *grams*. (Ex. 15–21.)

Technical Words

Valence state—the compounds or ions in which any given element has some specified valence number.

Anode, p. 235. **Cathode,** p. 235.

Chlorination—a reaction between chlorine and any compound, usually either by direct addition or substitution.

Exchange reaction, p. 239. **Substitution,** p. 239.

Summary

Try to remember the *names* of the products formed in each important reaction, with their *formulas* and something of the *conditions* under which each reaction takes place. Do not attempt to memorize the equations themselves.

Turn to the table of valence states on p. 232, and determine whether you can describe conditions and write equations for most of the 27 numbered reactions. All but the more complicated ones may readily be balanced by inspection.

► § 194. Salt content of the ocean. Other chlorides in ocean water. Chloride deposits in nature.

► § 195. Range of valence numbers for chlorine. A compound to illustrate each valence state.

► § 196. Preparation of hydrogen chloride. Why it fumes in the air.

Distinction between hydrogen chloride and hydrochloric acid. Reaction of hydrogen chloride with ammonia.

Six reactions in which hydrogen chloride serves as a typical acid.

► § 197. Two successive reactions, leading from common salt to hydrogen chloride and from this to chlorine.

► § 198. What happens at each electrode in the electrolysis of common salt. A cross section of an electrolytic cell, indicating materials used.

► § 199. Physical properties of chlorine. A practical antidote for chlorine fumes.

► § 200. Examples of different elements that combine directly with chlorine. What determines whether an element will display its lower or its higher valence, in combining or otherwise reacting with chlorine.

► § 201. The reaction of chlorine with solutions of a bromide or iodide. Contrast this with the reaction of chlorine with free bromine or iodine.

► § 202. An example of each of the chief ways in which chlorine reacts with hydrocarbons.

► § 203. What happens when chlorine dissolves in water. Evidence for the presence of three separate dissolved substances in the solution thus formed.

► § 204. Two substances that react with chlorine to produce hypochlorite. Reasons for keeping the solution cold, in these reactions.

How bleaching powder is made. What happens when bleaching powder is exposed to the air.

§ 205. What must be done to a dilute solution of a hypochlorite to render it of use in bleaching. Name and formula of the substance produced when hypochlorous acid decomposes, losing water.

Two different ways in which a mixture of hypochlorite and chloride may behave on being acidified.

§ 206. How chlorates are commonly prepared. Two ways in which the abuse of chlorates may result in an explosion.

§ 207. How perchlorates are prepared, in the laboratory and commercially. Laboratory preparation of perchloric acid.

► § 208. Chief uses of chlorine.

► § 209. How one may determine, by inspection of an equation, what relative volumes of two or more gases are concerned in that reaction.

An example of how one may determine what volume of a gas, under standard conditions, reacts with, results from, or produces a given weight of some other reactant.

Exercises

1. Check the valence number of chlorine in each of the compounds and ions in which chlorine is represented on p. 232 as having a valence number of +1.

2. Similarly, check the compounds and ions in which chlorine is represented as having a valence number of +5.

3. Similarly, for a valence number of +7.

4. Write non-ionic equations for six separate reactions in which hydrochloric acid serves as a typical active acid. Then replace the formula of each oxide, alkali, or salt by the formulas of the corresponding ions. Cancel out ions common to both sides of the equation, and so obtain the ionic equation for each of the six reactions.

5. Write an equation to show what is transferred and what ions are formed in the reaction of hydrogen chloride with ammonia.

6. Show how the formula Cl_2 enables one to find the density of chlorine gas, in comparison with that of air.

7. Write equations for burning in chlorine the eight metals named in § 200, item 2, indicating two possible products with the three metals last named.

8. Write an equation for the reaction of chlorine with carbon disulfide, CS_2, the products being carbon tetrachloride, CCl_4, and sulfur monochloride, S_2Cl_2.

9. Write equations for the production of phosgene, $COCl_2$, passing carbon dioxide over heated carbon (§ 60), then combining the product with chlorine, in the sunlight or in the presence of a catalyst.

10. Write and balance an equation for the reaction when methane is treated with a large excess of chlorine, all the hydrogen in the methane molecule being replaced by chlorine, the other product being hydrogen chloride.

11. Representing bleaching powder by the formula of its active ingredient, calcium hypochlorite, give an equation for converting it into sodium hypochlorite by a reaction in solution in which an insoluble carbonate is precipitated.

12. Write an equation for the reaction that takes place when a solution of calcium chlorate is treated with potassium chloride, one of the products of the reaction being precipitated.

13. When chlorine reacts with a cold solution of sodium carbonate (§ 204) compare the volume of the carbon dioxide liberated with that of the chlorine used.

14. When carbon disulfide vapor is treated with chlorine, to form carbon tetrachloride and sulfur monochloride, what volume of chlorine will be needed and what volume of each product will be obtained, for each liter of carbon disulfide vapor used? 300, 100

15. What volume of chlorine gas is needed to produce sufficient hydrogen chloride to neutralize 1 mole of calcium hydroxide?

16. In producing 1 kg of aluminum chloride by the reaction of § 200, what volume of chlorine is needed? 252

17. What volume of oxygen under standard conditions can be obtained by strongly heating 12.25 grams of potassium chlorate? 336

18. A 6 per cent solution of sodium carbonate has a density of 1.06 g/ml. What actual weight of sodium carbonate (§ 293) is contained in 100 ml of this solution? What volume of chlorine gas under standard conditions is needed to react with it? 636, 134

19. How many liters of chlorine gas, under standard conditions, are needed to react with 1 mole of calcium bromide?

20. What volume of carbon dioxide is evolved when 1 mole of sodium carbonate is treated with an excess of chlorine? 224

21. The vapor of phosphorous trichloride is found to have 4.75 times the density of air at the same temperature. Is the formula PCl_3 or P_2Cl_6?

Chapter 17

THE PERIODIC TABLE

► 210. Groups of Related Elements

A century ago, about fifty-five of the ninety-six elements known today had already been discovered. This was a sufficient number to permit the classification of the elements into groups of elements, all the members of any one group being very much alike in their chemical behavior. Thus lithium, sodium, and potassium were observed to form a *triad* [1] of elements, the *alkali metals*, of similar chemical behavior, and remarkable in being so light that they float on water. In the same way, chlorine, bromine, and iodine formed a triad of elements, the *halogens* (*Greek:* salt formers), so named because they react directly with the alkali metals to form salts, including common salt, NaCl. Other triads were easily recognizable.

The discovery of rubidium and cesium in 1860, with properties that classed them with the three alkali metals already known, proved that a group of related elements need not be limited to three, but perhaps might include five elements or more. Then Lothar Meyer, in Germany, and Mendeleev,[2] in Russia, almost simultaneously (1869) made a very important observation: *A list of elements, in the order of increasing atomic weight, may be tabulated in such a manner as to place chemically similar elements in the same vertical column.* (Ex. 1.)

Mendeleev's arrangement of the elements, shown on the opposite page, was called a *Periodic Table.* The name indicates that we come back to chemically similar elements at definite periods or intervals, as we pass through the table from the element of lowest atomic weight (hydrogen) to the element of highest atomic weight (uranium). All the elements in any given vertical column are of very similar chemical behavior.

[1] A *triad* means a group of three.

[2] This is spelled according to the system for the transliteration of Russian words that has been adopted by the American Chemical Society. Pronounce, *Men-dyěl-yā'-yěf*, with *yā* as in Yates, *yě* as in yet.

PERIODIC TABLE Mendeleev's form, brought down to date

Group:	1		2		3		4		5		6		7		8A or 0	8B		
Oxide:	R_2O		RO		R_2O_3		RO_2		R_2O_5		RO_3		R_2O_7			RO_4		
Hydride:	RH		RH_2		RH_3		RH_4		RH_3		RH_2		RH		Inert Gases	Transition Triads		
Series	A	B	A	B	B	A	B	A	B	A	B	A	B	A				
1	1 H 1.008														2 *He 4.00			
2	3 Li 6.94		4 Be 9.02			5 B 10.82		6 C 12.01		7 N 14.01		8 O 16.000		9 F 19.00	10 *Ne 20.18			
3	11 Na 23.00		12 Mg 24.32			13 Al 26.97		14 Si 28.06		15 P 30.98		16 S 32.06		17 Cl 35.46	18 *A 39.94			
4 →	19 K 39.10	29 Cu 63.57	20 Ca 40.08	30 Zn 65.38	21 *Sc 45.10	31 *Ga 69.72	22 Ti 47.90	32 *Ge 72.60	23 V 50.95	33 As 74.91	24 Cr 52.01	34 Se 78.96	25 Mn 54.93	35 Br 79 92	36 *Kr 83.7	26 Fe 55.85	27 Co 58.94	28 Ni 58.69
5 →	37 Rb 85.48	47 Ag 107.88	38 Sr 87.63	48 Cd 112.41	39 Y 88 92	49 In 114.76	40 Zr 91.22	50 Sn 118 70	41 Cb 92.91	51 Sb 121.76	42 Mo 95.95	52 Te 127.61	43 * ?	53 I 126.92	54 *Xe 131.3	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7
6 →	55 Cs 132.91	79 Au 197.2	56 Ba 137.36	80 Hg 200.67	57-71 Rare Earths	81 Tl 204.39	72 *Hf 178.6	82 Pb 207.21	73 Ta 180.88	83 Bi 209.00	74 W 183.92	84 *Po —	75 *Re 186.31	85 ? —	86 *Rn 222	76 Os 190.2	77 Ir 193.1	78 Pt 195.23
7	87 * —		88 *Ra 226 05		89-96 Actinide Elements								Arrows indicate rows occupied by the post-transition elements (those having inner electron shells complete)					

Lanthanide Elements (Rare earth series)	57 La	58 Ce	59 *Pr	60 *Nd	61 * ?	62 *Sa	63 *Eu	64 *Gd	65 Tb	66 *Dy	67 *Ho	68 Er	69 *Tm	70 *Yb	71 *Lu
Actinide Elements	89 *Ac	90 Th	91 *Pa	92 U	93 *Np	94 *Pu	95 *Am	96 *Cm							

$\underbrace{\text{93 *Np \quad 94 *Pu \quad 95 *Am \quad 96 *Cm}}_{\text{Synthetic}}$

► 211. Long and Short Periods

Mendeleev gave the name *periods* to the intervals that must be passed through between any given element and the next closely related element—between sodium, for example, and potassium; or between bromine and iodine.

The successive periods of the table are best counted as beginning with hydrogen or an alkali metal (Column 1A), and as ending with an *inert gas* (Column 0). Observe that the periods are not all of the same length. We have (1) an *initial period* of two elements, hydrogen and helium; then (2) a *short period* of eight elements, beginning with lithium and ending with neon; then (3) *another short period* of eight elements, beginning with sodium and ending with argon.

Following this we have (4) a *long period* of eighteen elements, beginning with potassium, running through two complete rows of Mendeleev's table, and ending with krypton; then (5) *another long period* beginning with rubidium, running through two rows of the table, and ending with xenon. Next, we have (6) an *extra-long period* of thirty-two elements, beginning with cesium, running through two rows of the table, and ending with radon. In this period there occur 15 elements, the rare-earth elements, all in the same position in the table. Finally, there is (7) an *incomplete period* of ten elements, ending with curium, Cm.

Observe that the number of elements in the different periods of the Periodic Table are given by $2 \times 1^2 = 2$, $2 \times 2^2 = 8$, $2 \times 3^2 = 18$, and $2 \times 4^2 = 32$. We shall let this fact remain as spice to the reader's curiosity, until its explanation turns up in a later chapter.

► 212. Main Groups and Subgroups

Since the successive periods (inferred from the actual properties of the elements) are not all of the same length, but may be two, eight, eighteen, or thirty-two elements, Mendeleev encountered difficulties in fitting all the elements into an eight-column table. This was accomplished, as we have seen, *by letting certain periods extend over two successive rows of the table.* Even then we have had to crowd the fifteen rare-earth elements, which are actually very much alike in their properties, into a single place in the table. To scatter them through a number of successive columns of the table would place them beneath elements that they fail to resemble at all. The final eight elements are also so much alike that they are best regarded as occupying a single place in the table.

The different sets of chemically similar elements, in successive vertical columns of the table, are called *groups or families.*

The first few and *the last few* elements in each of the long periods of Mendeleev's table were placed immediately below corresponding elements in the preceding short groups. These are the columns headed 1A, 2A, 6A, 7A, etc. They are often called the *main-group elements,* including chiefly *light metals* and *non-metals.*

The elements in the middle part of the long periods are placed in separate groups (1B, 2B, etc.) in the table. These *subgroup elements* include most of the heavy metals (§ 213) and the rare-earth metals. Near the middle of each of the three long periods is a group of three successive elements (Fe, Co, Ni, for example) which are so closely related that they are given a single place in the table (in column 8). These are the *transition triads.*

In groups 3 and 4, the main group (A) and the subgroup (B) are very *closely related* in all their important properties; but near the margins of the table (in Groups 1 and 2, or in 5 and 6) the main groups and subgroups are but *slightly related,* resemblance consisting chiefly in the formation of compounds of similar formulas. Thus sodium (1A) forms NaCl and silver (1B) forms AgCl; chlorine (7A) forms potassium perchlorate, $KClO_4$, and manganese (7B) forms potassium permanganate, $KMnO_4$. Otherwise there is little resemblance between sodium and silver, or between chlorine and manganese. (Ex. 2.)

► 213. Four Classes of Elements

The *light metals* include the alkali metals (Column 1A), the alkaline-earth metals (Column 2A), and the rare-earth metals (certain positions in Column 3A). They are all excellent conductors of heat and electricity. Chemically, their most important characteristic is the readiness with which their atoms lose electrons, thus forming *positive ions* (cations). (Ex. 3.)

The *heavy metals* include most of the elements in the B groups (subgroups) of the Periodic Table, familiar examples being iron, copper, zinc, and mercury. Most of them are good conductors of heat and electricity. Though their atoms can be made to part with electrons, thus producing *positive ions* (Fe^{++}, Fe^{+++}, Zn^{++}, etc.), this happens less readily than with the alkali metals. Many heavy metals combine with oxygen, fluorine, and certain groups of non-metallic atoms, to form negatively charged ions (anions), such as MnO_4^-, $Fe(CN)_6^{---}$, and $Co(NO_2)_6^{---}$. (Ex. 4.)

The *inert gases* (Column 0) are included among the non-metals. They differ from other elements in their almost complete inability to form chemical compounds. Their atoms do not even combine in pairs to form diatomic molecules. Thus they are represented by the *monatomic* formulas He, Ne, A, etc., whereas hydrogen is H_2 and oxygen is O_2. The chemistry of the inert gases therefore might almost be summarized by saying, "There is none." What we know of them is really physics. (Ex. 5.)

The remaining *non-metals* (nitrogen, oxygen, chlorine, etc.) occupy the A groups in the upper right-hand part of the Periodic Table. They are poor conductors of heat and electricity. Most of them are *gases*, or *solids that melt at temperatures not very much above room temperatures.* Most non-metallic atoms (either alone or when united to atoms of small radius, such as those of oxygen and fluorine), accept and retain extra electrons from an outside source, thus forming *negative ions* (anions). (Ex. 6.)

► 214. Another Form of the Periodic Table

In another form of the Periodic Table, shown on the opposite page, the elements have been arranged in eighteen columns, corresponding to the periods that contain eighteen elements. With this arrangement the B groups (heavy metals and rare-earth metals) are all found together in the middle part of the table. Slanting lines of different thicknesses represent the degree of resemblance between the main groups (A) and the subgroups (B)—greatest for Groups 3 and 4, less for groups immediately preceding and following these, and least for Groups 1 and 6. This eighteen-column table is repeated, facing the back cover of this book. Hereafter, reference will always be to this form of the table.

Among the heavy metals, in the middle part of the 18-column table, closely related elements are not only those in the same vertical column, but also adjoining elements in the same horizontal row. Thus manganese is closely related to chromium and iron. Iron, cobalt, and nickel form a *triad* of closely related elements. So do elements 44, 45, 46, and elements 76, 77, 78.

Though the elements in the Periodic Table are in general arranged in the order of increasing atomic weight the reader will discover four places in the table in which the atomic weight actually falls off a trifle in passing from one element to the next. In other words, there are four places in the table in which the order of increasing atomic weight has to be reversed in order to keep related elements in the same

PERIODIC TABLE

Atomic Number →
Atomic Weight →
Electron Orbits →

The different thicknesses of the sloping lines represent different degrees of similarity between A-Groups and B-Groups. Thus IVA and IVB are very closely related, but 1A and 1B only slightly.

The scale at the bottom of the table gives the most important valences (valence numbers) for each element. A valence number in excess of +3 is usually shown only when the given element is in association with another (commonly oxygen); Mn, for example, in permanganate-ion, MnO_4^-, has a valence number of +7

LIGHT METALS — TRANSITION HEAVY METALS — HEAVY METALS — NON-METALS — INERT GASES

New electron-group begun → Next-inner electron-group built up to 18 → Outer electron-group built up to 8

Figures in bold-faced type indicate completed electron-groups.

0	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
	1 H 1.0078 K 1																	2 He 4.002 K **2**
(He)	3 Li 6.94 KL **2**·1	4 Be 9.02 KL **2**·2											5 B 10.82 KL **2**·3	6 C 12.00 KL **2**·4	7 N 14.008 KL **2**·5	8 O 16.000 KL **2**·6	9 F 19.00 KL **2**·7	10 Ne 20.183 KL **2·8**
(Ne)	11 Na 22.997 KLM **2·8**·1	12 Mg 24.32 KLM **2·8**·2											13 Al 26.97 KLM **2·8**·3	14 Si 28.06 KLM **2·8**·4	15 P 31.02 KLM **2·8**·5	16 S 32.06 KLM **2·8**·6	17 Cl 35.457 KLM **2·8**·7	18 A 39.944 KLM **2·8·8**
(A) KL **2·8**	19 K 39.096 MN 8·1	20 Ca 40.08 MN 8·2	21 Sc 45.10 MN 9·2	22 Ti 47.90 MN 10·2	23 V 50.95 MN 11·2	24 Cr 52.01 MN 13·1	25 Mn 54.93 MN 13·2	26 Fe 55.84 MN 14·2	27 Co 58.94 MN 15·2	28 Ni 58.69 MN 16·2	29 Cu 63.57 MN **18**·1	30 Zn 65.38 MN **18**·2	31 Ga 69.72 MN **18**·3	32 Ge 72.60 MN **18**·4	33 As 74.91 MN **18**·5	34 Se 78.96 MN **18**·6	35 Br 79.916 MN **18**·7	36 Kr 83.7 MN **18·8**
(Kr) KLM **2·8·18**	37 Rb 85.44 NO 8·1	38 Sr 87.63 NO 8·2	39 Y 88.92 NO 9·2	40 Zr 91.22 NO 10·2	41 Cb 93.3 NO 12·1	42 Mo 96.0 NO 13·1	43 ? 99 ± NO 13·2	44 Ru 101.7 NO 15·1	45 Rh 102.91 NO 16·1	46 Pd 106.7 NO 18·0	47 Ag 107.880 NO 18·1	48 Cd 112.41 NO 18·2	49 In 114.76 NO 18·3	50 Sn 118.70 NO 18·4	51 Sb 121.76 NO 18·5	52 Te 127.61 NO 18·6	53 I 126.92 NO 18·7	54 Xe 131.3 NO 18·8
(Xe) KLM **2·8·18**	55 Cs 132.91 NOP 18·8·1	56 Ba 137.36 NOP 18·8·2	57-71 Rare Earth Metals	72 Hf 178.6 NOP **32**·10·2	73 Ta 181.4 NOP **32**·11·2	74 W 184.0 NOP **32**·12·2	75 Re 186.31 NOP* **32**·13·2	76 Os 191.5 NOP* **32**·14·2	77 Ir 193.1 NOP* **32**·17·0	78 Pt 195.23 NOP* **32**·17·1	79 Au 197.2 NOP **32·18**·1	80 Hg 200.61 NOP **32·18**·2	81 Tl 204.39 NOP **32·18**·3	82 Pb 207.22 NOP **32·18**·4	83 Bi 209.00 NOP **32·18**·5	84 Po 210 NOP **32·18**·6	85 ? NOP **32·18**·7	86 Rn 222 NOP **32·18·8**
(Rn) KLMN **2·8·18·32**	87 ? OPQ 18·8·1	88 Ra 225.97 OPQ 18·8·2	89-96 Actin- ide Metals															

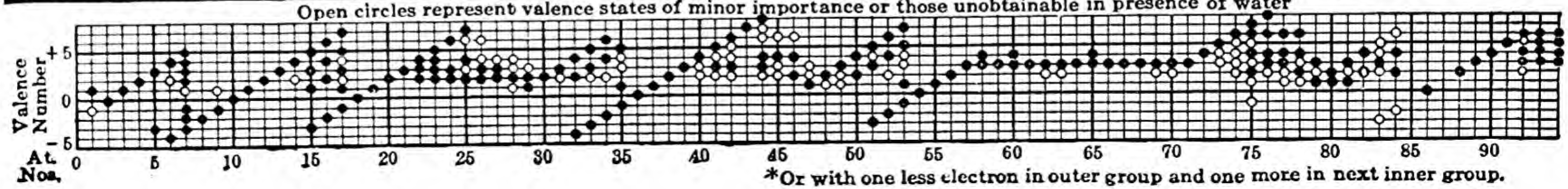
THE RARE EARTH METALS ARE:

57 La	58 Ce	59 Pr	60 Nd	61 ?	62 Sa	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP
18·9·2	19·9·2	20·9·2	22·8·2	23·8·2	24·8·2	25·8·2	25·9·2	26·9·2	28·8·2	29·8·2	30·8·2	31·8·2	32·8·2	32·9·2

THE ACTINIDE METALS ARE:

89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm
227 ±	232.12	231	238.14	Synthetic Elements			
OPQ	OPQ	OPQ	OPQ				
18·9·2	18·10·2	18·11·2	18·12·2				

Open circles represent valence states of minor importance or those unobtainable in presence of water



*Or with one less electron in outer group and one more in next inner group.

vertical column. (One of these four is among the rare-earth elements.) (Ex. 8.)

► 215. Using the Table to Predict New Elements

To keep related elements together in the same vertical column, Mendeleev had to leave a few blank spaces in the table, to represent undiscovered elements. He made bold to predict the properties of several of these in advance of their discovery, and his predictions, in every instance, were later verified with remarkable accuracy.

Predictions by Mendeleev, 1871	*Observations by Winkler*, 1886
EKA-SILICON	GERMANIUM
Atomic weight, 72.	Atomic weight, 72.3.
Density, 5.5.	Density, 5.47.
Atomic volume,* 13.	Atomic volume, 13.2.
Color, dirty gray.	Color, grayish white.
On being heated in air gives a white powder, EsO_2.	Gives a white oxide, GeO_2.
Only slightly affected by acids.	Not affected by HCl.
No pronounced action by alkalies.	Solutions of alkalies have no action. Oxidized in presence of fused alkalies.
Reduced from EsO_2 or K_2EsF_6 by Na.	Reduced from GeO_2 by carbon; from K_2GeF_6 by Na.
Oxide, EsO_2 refractory, density 4.7.	GeO_2, refractory, density 4.703.
$EsCl_4$, liquid, b.p. 100°C, density 1.9.	$GeCl_4$, liquid, b.p. 86°C, density 1.887.
EsF_4, not a gaseous compound.	$GeF_4 \cdot 3H_2O$, white solid.
Forms $Es(C_2H_5)_4$, b.p. 160°C, density 0.96.	$Ge(C_2H_5)_4$, b.p. 160°, density slightly less than that of water.

* The volume of a gram atom, in cubic centimeters.

In the table on p. 251, elements marked with a star have been discovered since the date of Mendeleev's original table and have been fitted into places where he left blanks. It will be noted that he overlooked an entire column of elements, the inert gases, which were discovered nearly thirty years later (1894) and are now given a place at the extreme right of the table.

► 216. The Work of Moseley. The Periodic Law

Mendeleev and his immediate successors had no way of telling how many elements still remained to be discovered. They simply left vacant places in the Periodic Table whenever this procedure helped them to get elements of similar properties into the same vertical column. But in 1913 a young British physicist, Henry G. J. Moseley,

then only 26,[3] devised a method for determining how many elements there are from the beginning of the table to any specified element. The number of elements still to be discovered could then readily be counted.

Moseley placed samples of the different elements within an evacuated tube, where they were used as *targets*, to be bombarded by a swift-moving stream of electrons. By this device all the then-known elements except the very lightest could be made to emit X-rays. As he passed forward through the Periodic Table from one element to the next, Moseley discovered that these rays gradually change their character. So the *order* of the elements in the table was for the first time established beyond any doubt, by a method that was quite independent of atomic weights and of the rough comparison of properties which previously had to serve.

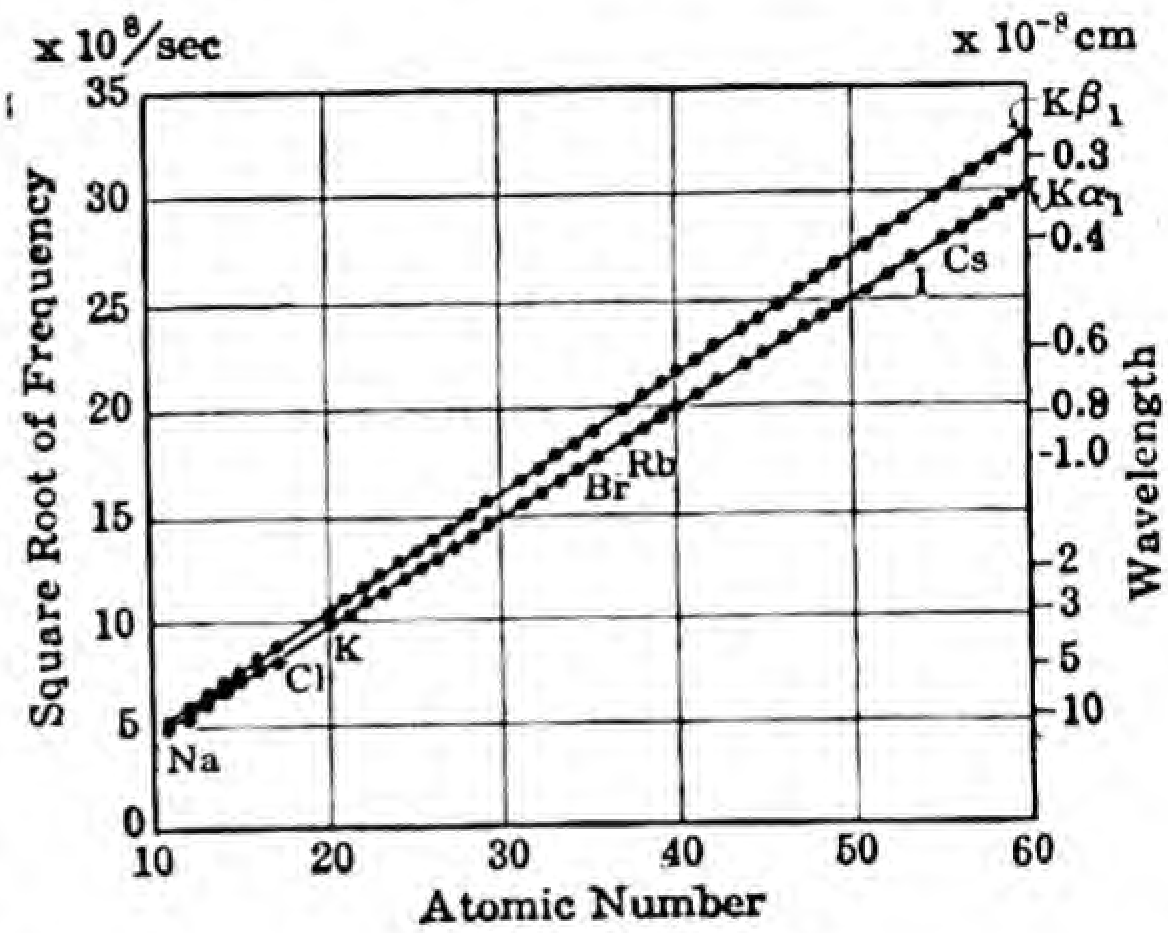


FIG. 85. Moseley's Law. The square root of the frequency (for any given line of the X-ray spectrum of an element) is very nearly proportional to the atomic number. The two lines in the figure represent square root of frequency, plotted against atomic number, for the spectral lines designated as $K\alpha_1$, and $K\beta_1$.

From a study of the X-rays emitted by any element, Moseley was able to assign to it a definite *atomic number*—a whole number which gives each element a definite *sequence position* in the table, counting forward from hydrogen (atomic number, 1) to curium (atomic number, 96). He showed, for example, that calcium is the twentieth element and iron the twenty-sixth. *Moseley's Law* is summarized in Fig. 85.

In modern versions of the Periodic Table the atomic number is usually placed above or before the symbol of each element, and the atomic weight beneath the symbol. Turn to either of the forms on pp. 251 and 255, and observe how the atomic number progresses steadily, one unit at a time, from hydrogen to uranium. Observe also that the atomic weight of an element in the early part of the table is almost exactly twice its atomic number. But in later parts of the

[3] Two years later Moseley was killed in the disastrous assault at Gallipoli, the approach to the Dardanelles.

table the atomic weight is always considerably more than twice the atomic number. (Ex. 9.)

The four elements of highest atomic number (Nos. 93 to 96) were first produced from other elements, as related in §§ 593, 594. For this reason they are sometimes termed *synthetic elements.* The same is true of Nos. 43, 61, 85, 87, all of which may perhaps not occur in nature, because their atoms are unstable.

As new elements are hereafter confirmed or discovered, within the limits of the present table or beyond uranium (§ 593), the place of each in the table will be established by its atomic number, deduced from a study of the X-rays that it emits, without much regard to its atomic weight. Atomic number is fundamental, for we shall later find (§ 231) that it tells us something definite about the internal structure of an atom of that kind; whereas atomic weight is somewhat accidental, since it depends on the proportions in which the isotopes of the element (§ 35) happen to be intermingled.

The regularities expressed by the Periodic Table may therefore best be summarized in terms of *atomic numbers:*

When the elements are arranged in the order of increasing atomic number, elements of similar properties occur at regular intervals of two, eight, eighteen, or thirty-two elements. This is a modernized statement of what is often called the *Periodic Law.*

► 217. Valence and the Periodic Table

In an earlier chapter we distinguished between *ionic valence,* which gives the charge on an ion, and *non-ionic valence.* We learned how to find the *valence number* of any atom (§ 171) when combined with others, by assuming that every hydrogen atom (except in metallic hydrides) has an arbitrary charge of $+1$, and every oxygen atom (except in peroxides) an arbitrary charge of -2.

In Mendeleev's form of the Periodic Table (p. 251) the formulas R_2O, RO, R_2O_3, etc., at the top of the table, show the *maximum number of atoms of oxygen* with which one atom of any element in the given column is ever found to combine, and hence reveal the maximum valence number in that column, *in combination with oxygen.* This maximum valence number evidently increases from 0 (the inert gases) to a maximum of $+7$ (the halogens, in Column 7). Then, with the transition triads (Column 8) it falls off irregularly (though advancing to $+8$ in OsO_4).

The maximum valence number, in combination with hydrogen, is given by the formulas RH, RH_2, RH_3, etc., at the top of the table.

This passes from 0 (the inert gases) to −4 (Group 4), then passes back to 0 with the next inert gas.

A property that rises then falls in a fairly regular way, with increasing atomic number, is called a *periodic property.* Valence number is obviously a good example. In the eighteen-column table (p. 255) all the most important valence numbers for each element are shown in the diagram at the bottom of the table. With iron, the twenty-sixth element, for example, the valence numbers indicated are +2, +3, and +6. This diagram also very plainly reveals that the maximum valence number for the successive elements first increases to a maximum, then decreases, then rises again. (Ex. 10.)

218. Melting Point and Atomic Volume

A second periodic property is shown in Fig. 86, which plots the *melting points* of the elements against atomic numbers. Observe that

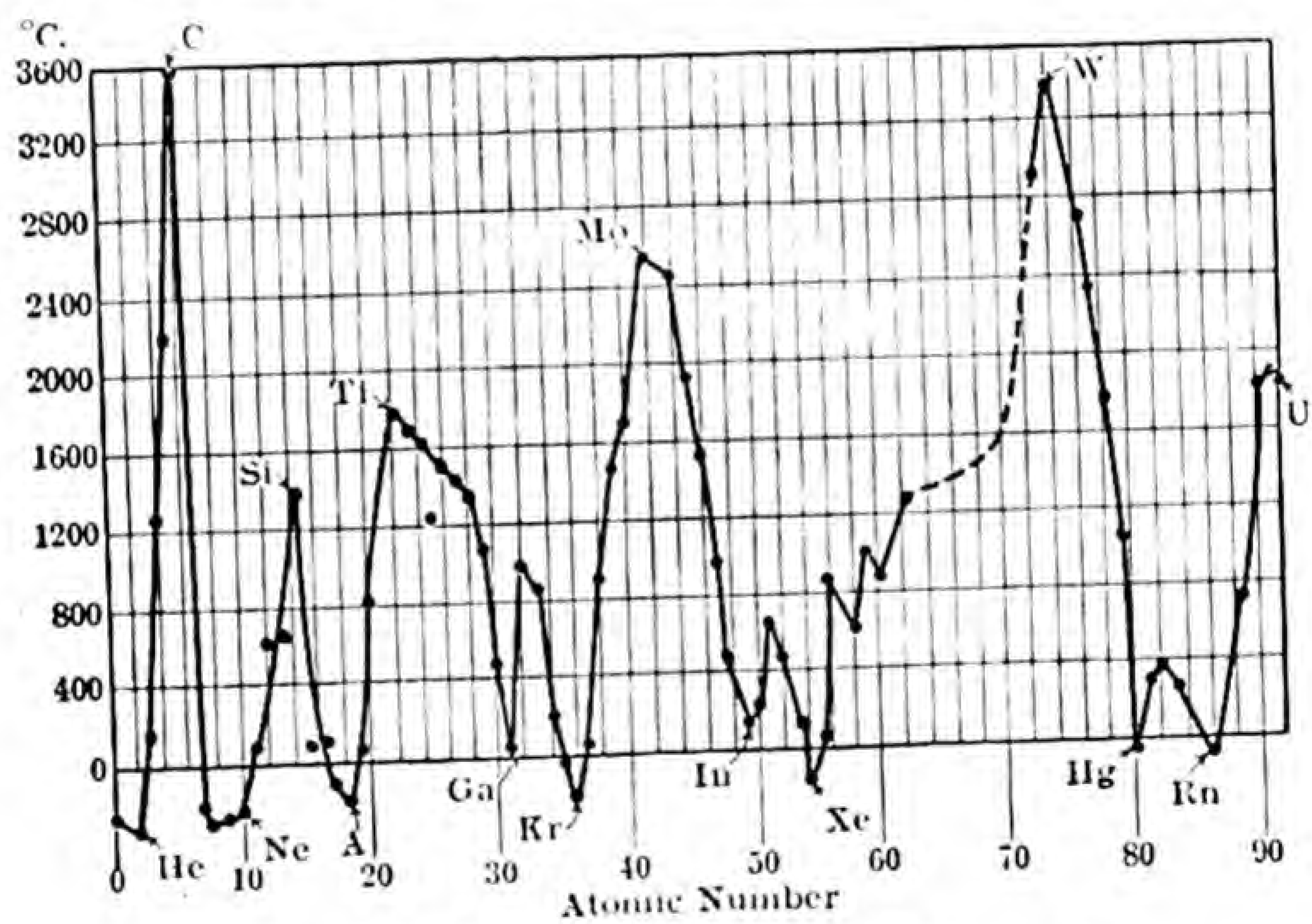


FIG. 86. Melting points of the elements.

the melting point is a minimum for the inert gases (except for neon, for which it is near a minimum). It is a maximum in Column 4 (for the lighter elements) and Column 6B (for the heavier elements).

Our third example of a periodic property, among many that might still be mentioned, is *atomic volume,* by which we mean *the volume of one gram atom of the element, in the solid condition.* Atomic volume is plotted against atomic number, in Fig. 87 (next page). We note an irregular rise and fall as we pass through the table. Observe also that this diagram gives very clear evidence that the successive periods are not all of the same length, but include 2, 8, 18 or 32 elements. (Ex. 11.)

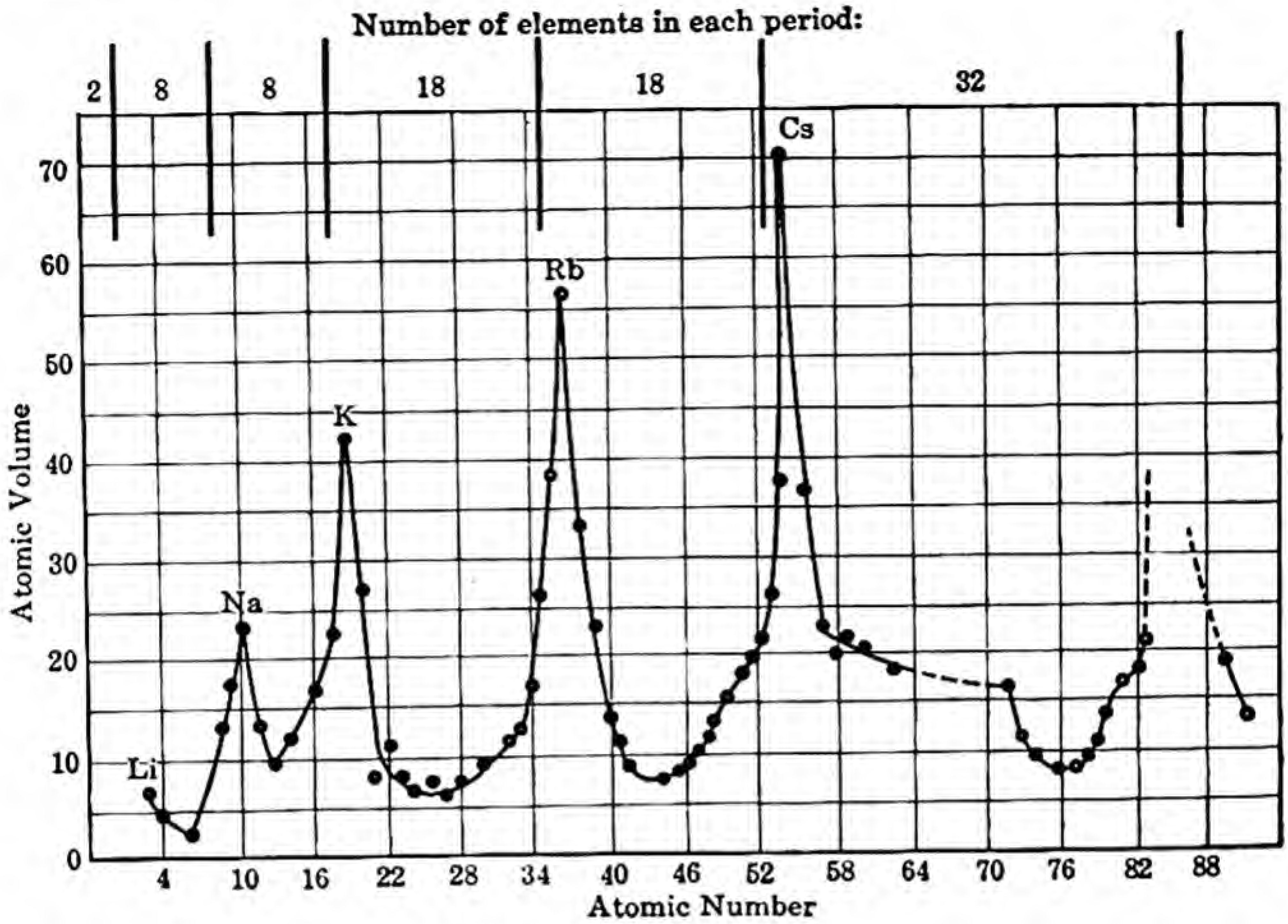


FIG. 87. Atomic volumes.

219. Chemistry's Major Riddle

The Periodic Table, in the years immediately following its inception, was responsible for the discovery of a number of new elements, and so rendered important service. It has always been helpful in suggesting resemblances that otherwise might not have been observed. For the student of chemistry, it economizes effort by permitting him to concentrate on a few elements that serve as types for the rest. Anyone familiar with the properties of the series of elements beginning with sodium and ending with argon can roughly predict those of most other important elements.

Nevertheless the table explains nothing. Instead, it presents a major riddle. As we pass through the table, elements of similar properties turn up at regular intervals. But, why? The answer must be that something is happening, *within the atom*, as we pass forward through the table, which at regular intervals brings us back to an internal structure somewhat like that which we had in the beginning. A riddle, here, indeed. The next chapter discloses the manner in which it has at length been solved.

TECHNICAL WORDS

Periodic Table, p. 250. **Triad,** p. 250. **Period,** p. 252.
Group or **family of elements,** p. 253.

Alkali metals—those in column 1A of the Periodic Table.
Alkaline-earth metals—those in Column 2A of the Periodic Table.
Halogens—the elements of Column 7A of the Periodic Table.
Main-group elements, p. 253. **Subgroup elements,** p. 253.
Transition triads, p. 253. **Light metals,** p. 253.
Heavy metals, p. 253. **Non-metals,** p. 254.
Inert gases—the elements of Column 0 of the Periodic Table.
Atomic number, p. 257. **Periodic property,** p. 259. **Atomic volume,** p. 259.

Summary

► § 210. Some examples of triads of related elements.
An observation due to Lothar Meyer and Mendeleev.
► § 211. Names given the horizontal rows of the Periodic Table. Number of elements in each of the seven successive rows.
► § 212. Distinction between main groups and subgroups. Which of these include the light metals, non-metals, heavy metals. Name given to triads in Column 8 of the Periodic Table. In which part of the table we find closest degree of relationship between main groups and subgroups.
► § 213. Names given the four chief classes of elements, with physical characteristics, and tendency to form compounds and ions.
► § 214. Sketch the eighteen-column table from memory, with the proper number of rows and columns, and locate from memory the positions of about twenty common elements.
► § 215. An example of the use of the Periodic Table for the prediction of the properties of undiscovered elements.
► § 216. How Moseley determined the position of undiscovered elements within the Periodic Table.
A statement of the Periodic Law in terms of atomic numbers.
► § 217. An indication of how the maximum valence number behaves in passing through the Periodic Table, for oxides and for hydrides.
The name given to any property that rises and falls in a regular way, when reviewing the elements in the order of increasing atomic number.
► § 218. In which columns of the Periodic Table maximum melting point and maximum atomic volume are encountered.
► § 219. What general conclusion may be drawn from the Periodic Table, with regard to the inner structure of atoms.

Exercises

1. From the Periodic Table on p. 255 determine which elements one would expect to be most closely related to vanadium (V).
2. Which elements are in the main group and which in the subgroup of the column headed with carbon?
3. Write electronic equations, representing an electron by *e*, to show the manner in which cations are formed from the second element of each of the first three columns of the Periodic Table.
4. Write electronic equations to show the manner in which ferrous ion and ferric ion, respectively, are produced from uncharged iron atoms.

5. Show that helium has twice the molecular weight of hydrogen, and that argon has $1\frac{1}{4}$ times the molecular weight of oxygen.

6. Write an electronic equation to show the manner in which a sulfide ion is produced from an atom of elementary sulfur.

7. What names are given to the families of elements to which elements 85 and 87, respectively, belong?

8. Locate at least two of the four places in the Periodic Table in which the atomic weight falls off a trifle in passing through the table from an element to the next following one.

9. Determine whether the most abundant elements in the earth's crust (§ 18) usually have odd or even atomic numbers.

10. What valence numbers are indicated for the element vanadium, in the diagram at the bottom of the Periodic Table?

11. The density of metallic vanadium is 5.7 g/cm^3. Its atomic weight is roughly 51. Calculate its atomic volume.

12. What valence numbers are indicated for the element vanadium, in the diagram at the bottom of the Periodic Table?

13. To speak with precision concerning the periodic arrangement of the elements the following terms should have definite meanings:

Metal	Atomic number
Period	Group or family of elements
Long period	Periodic property
Triad	Periodic law
Gram-atomic volume	Inert gas
Subgroup	Light metal
Rare-earth element	Synthetic element

Write sentences explaining or defining these terms.

14. From the position of radium in the Periodic Table determine its valence.

15. Which elements was Mendeleev himself able to predict and describe in detail in advance of their discovery?

16. If a new element, very similar to lead, should be discovered, where would you place it in the Periodic Table?

17. Electric furnaces are often wound with tungsten resistance wire. Consult the Periodic Table to determine what other elements might be worth trying as substitutes for tungsten.

Chapter 18

WITHIN THE ATOM

► 220. Becquerel's Experiments

To guess what the internal structure of atoms may be, and how it is modified as we pass through the Periodic Table, may seem to be quite hopeless. Yet the problem is on the way toward being solved, with the aid of evidence from many different sources. First to be considered is that afforded by the discovery that *the atoms of certain elements* (the radioactive elements) *are unstable, decomposing into fragments that we can separate and identify.*

It all began with the physicist Henri Becquerel, in Paris (1896). The scientific world had just been stirred by Roentgen's discovery of X-rays. Becquerel, and his father before him, had long been interested in *phosphorescent* minerals and salts—those that continue for a time to glow faintly in the dark, after being exposed to bright sunlight. He thought that such materials might emit not only visible light, when phosphorescing, but perhaps invisible rays as well. These might then be capable of penetrating black paper and affecting a photographic plate, in the same manner as X-rays had just been found to do.

The experiment failed with all the many substances tried, with one exception, a salt of uranium. This was found to give off invisible penetrating rays, even without previous exposure to sunlight. Furthermore, all uranium salts were found to do so *in exact proportion to their content of the element uranium.* Whether they were phosphorescent or not made no difference.

► 221. The Electroscope

Becquerel discovered that the rays emitted by uranium salts, like cathode rays and X-rays, cause air to become a conductor, and for the same reason, in brief, because they *ionize* the air. The effect is best studied with an *electroscope*, shown in Fig. 88 (next page).

An electric charge is communicated to B, which is then turned until it touches the rod D, from which a pair of gold leaves, or a gold leaf

and a fixed plate, are suspended. Fine quartz fibers, coated with platinum, are sometimes used instead of gold leaves. *S* is an insulating block, usually of amber or sulfur. The gold leaves repel each other, and diverge, as a result of the electric charge.

Next, we place a sample of a uranium salt, or some other radioactive material, before the window of thin aluminum foil, at *A*. Some of the rays pass through the foil and ionize the air within the electroscope. The charge on the gold leaves is then gradually neutralized by ions of the opposite charge, attracted to the leaves from the surrounding air. In consequence, the leaves slowly fall together. From the rate at which they move, one may estimate the rate at which ions are being formed within the chamber and hence the quantity of radioactive material in the sample. (Elements are said to be *radioactive* when they continuously emit rays which discharge an electroscope.)

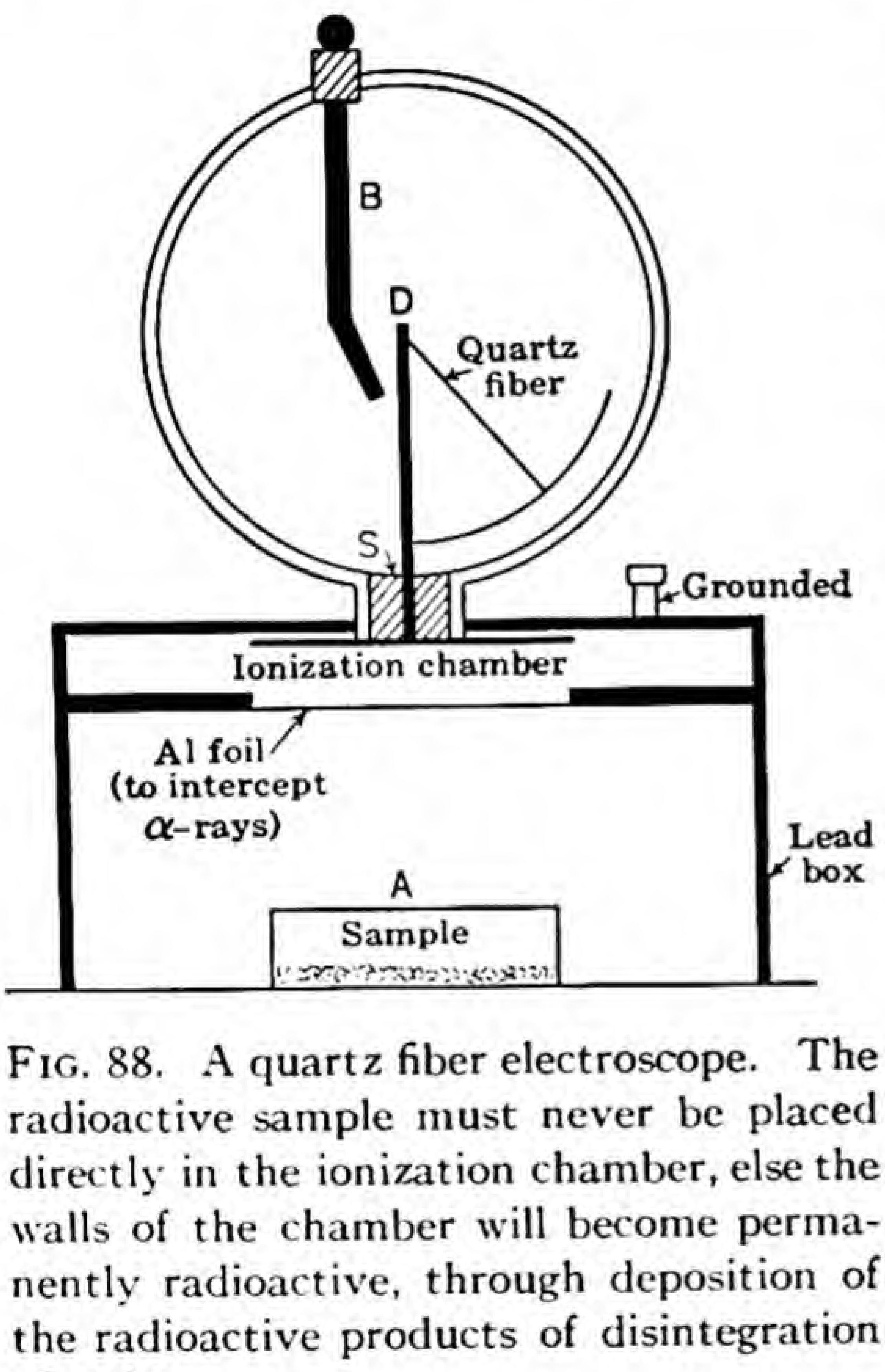


FIG. 88. A quartz fiber electroscope. The radioactive sample must never be placed directly in the ionization chamber, else the walls of the chamber will become permanently radioactive, through deposition of the radioactive products of disintegration of radon.

The electroscope, next to the ionization chamber or particle counter, § 226, is the most sensitive instrument ever devised for detecting and identifying small traces of matter. A millionth of a gram of uranium and still smaller quantities of certain other elements may be made to betray their presence by the increased rate of collapse of the leaves or fibers of an electroscope.

► 222. The Discovery of Radium and Polonium

Mme. Curie, a pupil of Becquerel, at his suggestion, examined a great number of minerals, and found that all thorium minerals, as well as all uranium minerals, are radioactive. The radioactive power of *artificially prepared salts* of these two elements, as measured by an electroscope, was found to be proportional to their content of the element uranium or thorium. Nevertheless, a uranium mineral called

pitchblende (from its black color) was much more strongly radioactive than could be accounted for by its content of uranium alone. Pitchblende was therefore suspected of containing some undiscovered element of greater radioactive power than uranium itself.

The result of some months of work was the discovery, not merely of one but of two new radioactive elements—*radium*, which resembled barium in being precipitable as an insoluble sulfate; and *polonium*, which resembled bismuth in being precipitable as an insoluble sulfide. By oft-repeated fractional crystallization of a mixture of barium chloride and radium chloride, Mme. Curie obtained a few milligrams of the latter salt, from several tons of ore, in nearly pure form.

► 223. Energy within Atoms

Radium was found to exhibit some interesting properties, never previously observed. Radium salts are faintly luminous in the dark. This is no ordinary phosphorescence, for it is not dependent on previous exposure to the light. Moreover, it seems to continue indefinitely, whereas ordinary phosphorescence gradually fades away. Radium continuously emits heat, at a rate sufficient to melt its own weight of ice every 45 minutes. Radium salts continue this prodigal emission of energy, day after day, and year after year, *apparently indefinitely!*

Does radium then *create* energy, out of nothing? Physicists would not believe that for a moment. If radium gave off energy continuously it could do that only because it contained a supply of energy in the beginning. Yet the total quantity of energy emitted by radium, over a period of years, was far greater than could be accounted for by any ordinary chemical change. Moreover, all radium salts emit energy continuously, *at a rate proportional to the amount of the element radium they contain*, and independently of whether the radium is present as a chloride, bromide, or in metallic form. This seems evidence that the emission of heat is a property of the radium atom.

Is something new and different, then, going on *within* the radium atom? Do the atoms of all the elements perhaps contain an unsuspected inner store of *atomic energy*, which the atoms of radium gradually release? As years went by this conviction grew.

► 224. Radium Atoms Disintegrate

Rutherford and Soddy (1903) accounted for the continuous emission of energy by radium and other radioactive atoms by assuming that their atoms, one by one, *disintegrate* or decompose into fragments

that are atoms of simpler elements (§ 573). In this process a part of the energy stored within the original unstable atoms is set free as heat.

In decomposing all of a 1-gram sample of radium, the total energy set free would be 2.4×10^9 calories—about as much as in burning 700 pounds of good anthracite coal! Similar impressive figures are obtained in estimates of the energy released in disintegration of other types of unstable atoms. We shall have more to say about that in Chapter 42.

► 225. Three Types of Rays

We have seen how the discovery of radium was the direct result of interest in rays and radiation, awakened by the discovery of X-rays. In their turn, the rays given off by uranium, radium, and thorium were eagerly examined. Were they a stream of material projectiles, or a stream of electrons, or a form of radiant energy, akin to X-rays? It was soon found that they were a mixture of all three. This was proved by placing the sample of the radioactive material in such a position that the rays needed to traverse a magnetic field. This resolved the rays into three separate beams, as in Fig. 89.

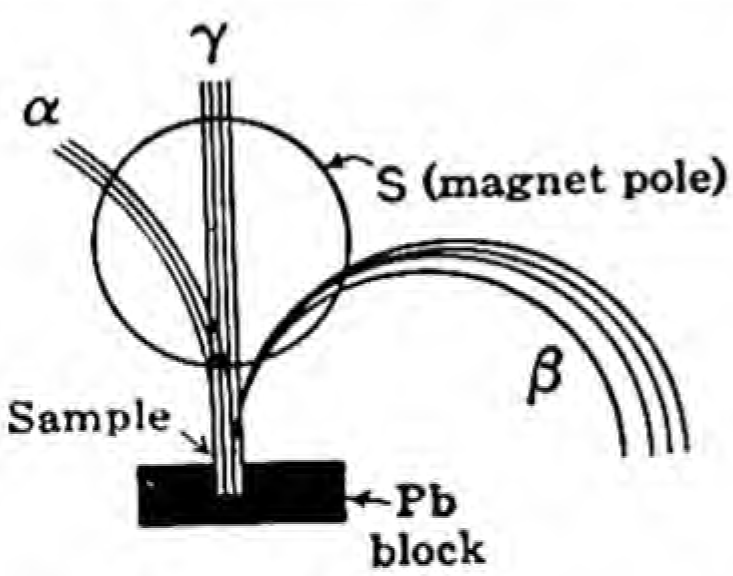


FIG. 89. Behavior in a magnetic field of the three types of rays emitted by radioactive substances.

Alpha (α) *rays* were deflected slightly in a direction that indicated that they carried positive charges of electricity. They were later shown to be positively charged material particles (§ 227). They have relatively slight penetrating power.

Beta (β) *rays* were deflected strongly in the opposite direction, and hence evidently carried negative charges of electricity. They were later shown to be swift-moving electrons.

Gamma (γ) *rays* were undeviated by the magnetic field and hence were either uncharged material particles or a beam of *radiant energy*.[1] Later work showed them to be radiant energy, similar to X-rays, but of even higher frequency. In consequence of their high frequency, they are very penetrating.

226. Counting Alpha Particles

The existence of separate *material particles* in a beam of alpha rays was confirmed by experiments in which these particles were indi-

[1] *Radiant energy* is visible or invisible light. It is propagated through empty space with a speed of 3×10^{10} cm (about 186,000 miles) per second. The *frequency* of radiant energy is the number of vibrations per second in the electromagnetic wave that guides or accompanies the radiant energy in its flight through space.

vidually detected or counted. When the particles strike a screen covered with crystalline zinc sulfide, each particle produces a tiny flash of light. Counting the flashes gives us a count of the particles themselves.

The alpha particles may also be counted with an electrical *particle counter* (Geiger counter), shown in Fig. 90. The radioactive sample, *S*, ejects alpha particles in all directions. A small window at *W* permits an occasional particle to enter the ionization chamber, *C*. It there collides with and ionizes a few molecules of air, rendering the air a conductor. There results a sudden rush of current through *C*, which is made to swing the pointer of a delicate electrometer, or else is amplified at *A*. Each alpha particle passing through the window *W* then announces its arrival by a sound in the telephone, *T*.

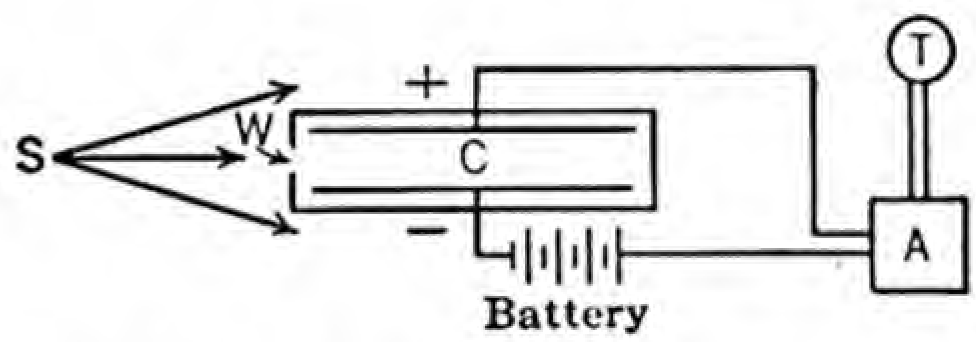


FIG. 90. A particle counter (Geiger counter).

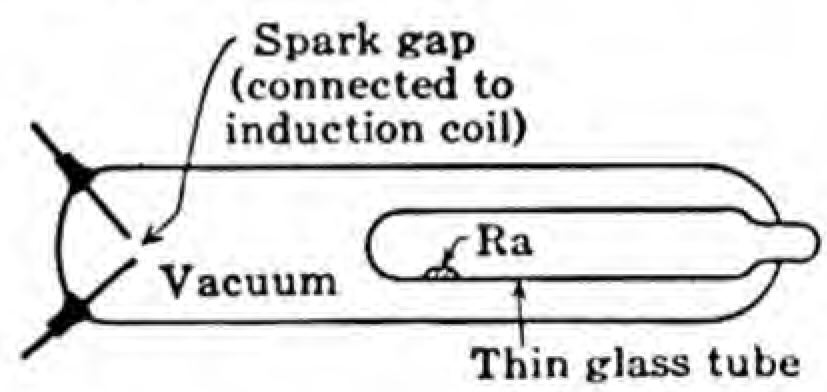


FIG. 91.

► 227. Alpha Particles are Doubly Charged Helium Ions

We may not only count alpha particles; we may also collect them and measure their total charge. Then, dividing the total charge by the number of particles, we obtain the charge on a single particle. It turns out to be twice the least charge ever encountered on any positively charged ion, namely, twice the charge on H^+ or Na^+.

Finally, *by measuring the curvature of the paths of alpha particles in traversing electric and magnetic fields*, it is possible to determine their *charge-per-unit-mass*. The charge having already been determined, the mass is easily calculated. It turns out to be *four times the mass of the hydrogen atom.*

Now *four* is the atomic weight of helium. The suspicion thus arises that alpha particles are really doubly positively charged helium ions, He^{++}. This suggestion was confirmed by Rutherford (1904), by demonstrating with a spectroscope (§ 234) the actual presence of helium in a tube into which alpha particles were permitted to penetrate through a thin glass wall (Fig. 91).

► 228. Fog Tracks

Fogs, mists, and clouds are really composed of liquid droplets, of microscopic size, stabilized in some way (§ 428). Such droplets are

usually formed by condensation upon dust particles or ions. An atmosphere free from dust and ions is one untroubled by mists and clouds (§ 350).

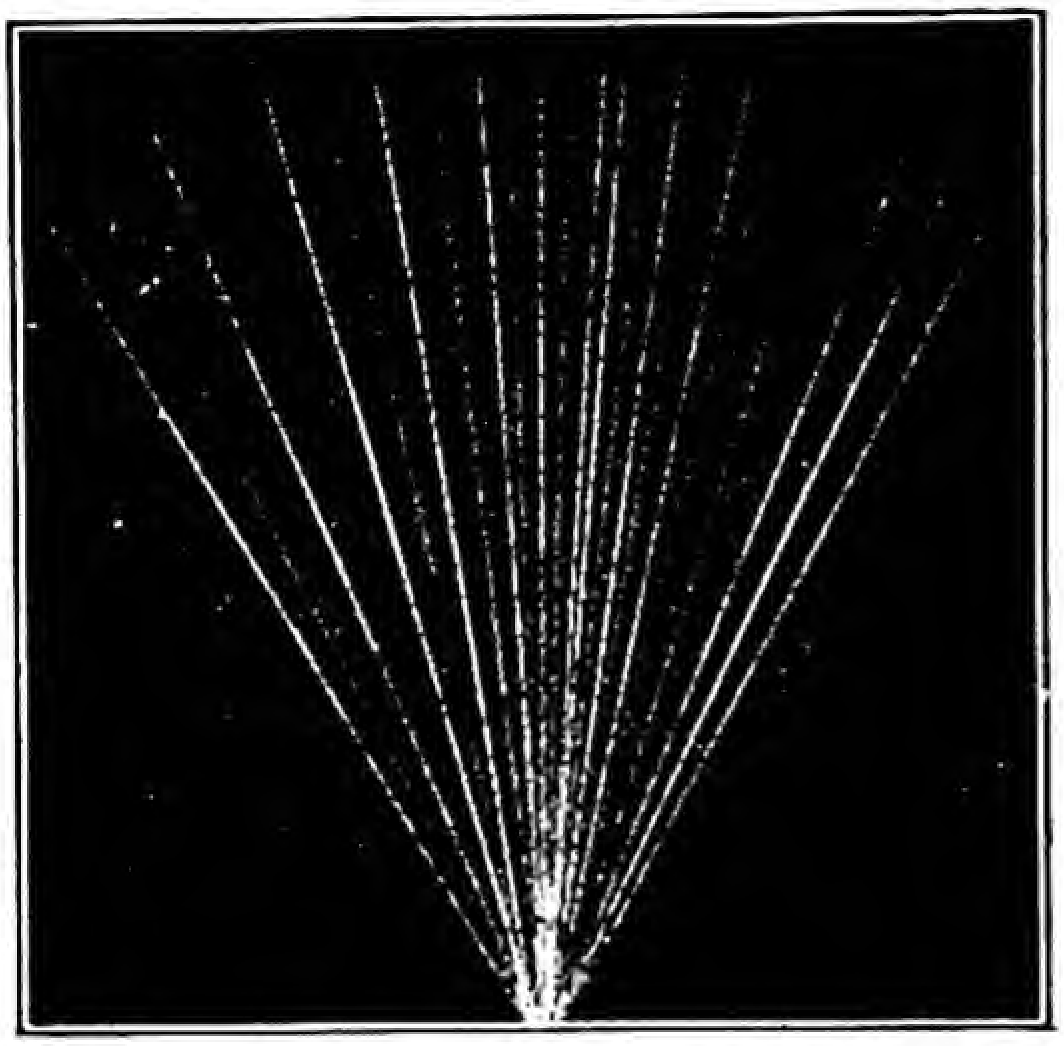
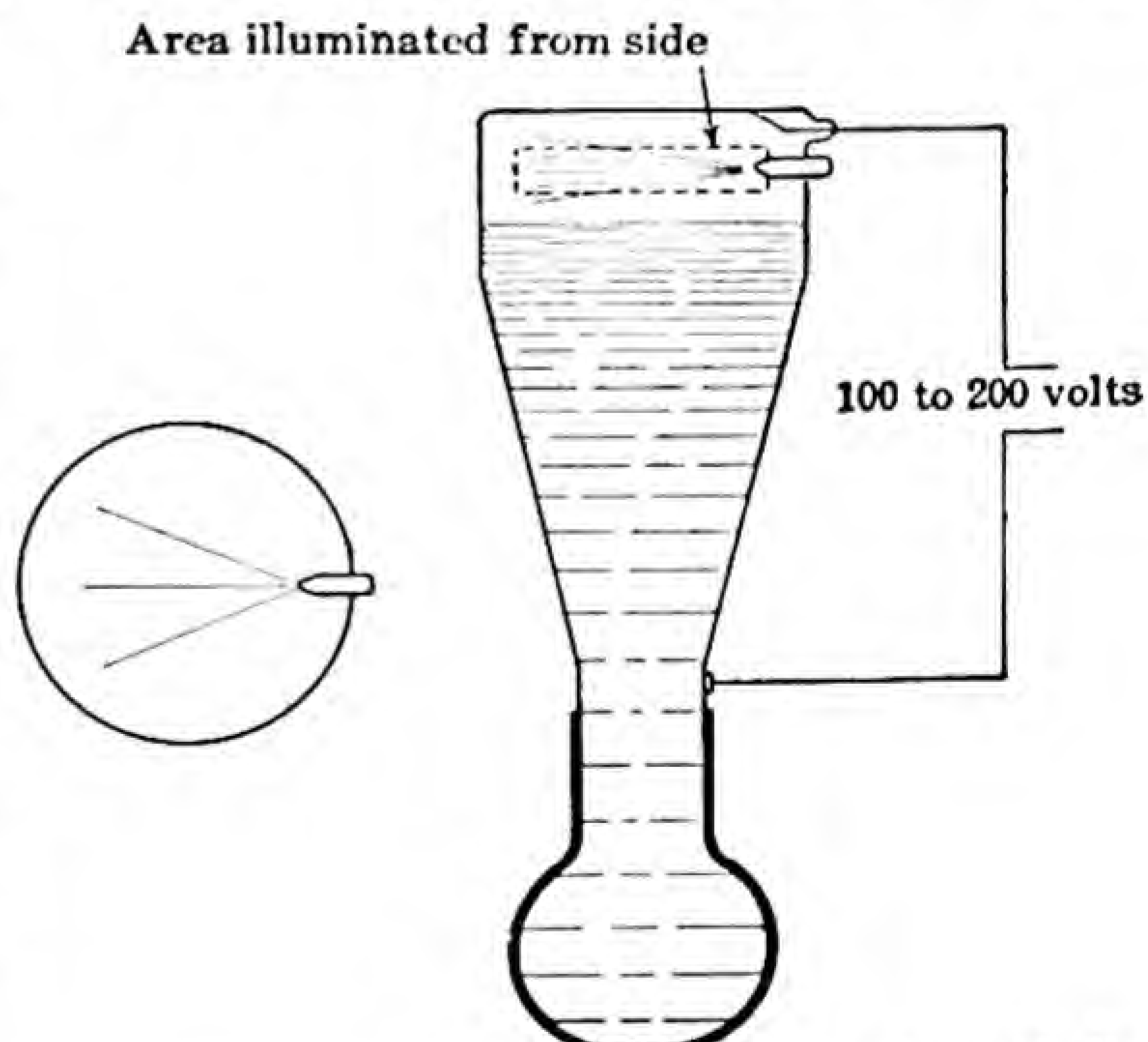


Fig. 92. Fog tracks produced by alpha particles in saturated air.

In this fact we find an excellent way for tracing the flight of alpha particles. We simply make them traverse a space containing air that is supersaturated with water vapor. Each alpha particle, in the course of its flight, passes through perhaps 150,000 molecules of air, causing these to lose electrons, which neighboring molecules gain. Thus a corresponding number of pairs of oppositely charged ions are produced. Immediately a microscopic droplet of water condenses about each ion as a nucleus. The path of the alpha particle is thus made evident as a streak of fog, which can be photographed (Fig. 92). By analogy, a locomotive, climbing a distant mountain slope, may be invisible, yet betray its path by a trail of condensed vapor.

The apparatus in which fog streaks are produced by swift-moving material particles, traversing air supersaturated with water vapor, is called a *Wilson Cloud Chamber*. Figure 93 shows a simplified cloud chamber with which anyone can produce and observe fog tracks produced by a trace of radioactive material.



Courtesy of Central Scientific Co.

Fig. 93. Demonstration alpha-ray-track apparatus. By compressing, then releasing, the rubber bulb at the bottom the air at the top of the chamber is supersaturated with moisture. A trace of radioactive material, behind a thin glass film, yields alpha particles that penetrate the film and produce cloud tracks. Applying a high voltage then clears the air of fog for the next observation.

Beta particles, because of their small mass and consequent small kinetic energy, do not produce so many ions as alpha particles do, and hence

leave only faint fog tracks, which waver about, as the beta particles are deflected from a straight-line path, in passing near the positively charged center of any atom (Fig. 94).

► 229. Every Atom Contains a Positively Charged Nucleus

Alpha particles, emitted by radioactive substances, are hurled off with such high velocities that they pass through thin sheets of metal or several inches of air, before they cease to ionize air and hence to produce fog tracks. The distance they traverse often proves to be at least a hundred thousand times as great as the average distance between the molecules of the air or metal through which the alpha particle has passed. Thus we have definite proof that the atoms or molecules of the air or metal are not solid, impenetrable structures, as the ancients and apparently even Dalton supposed. The alpha particle cuts right through them and speeds on, like an airplane through wisps of fog.

Fig. 94. Fog track made by a beta particle in supersaturated air.

Nevertheless, alpha particles, now and then, are deflected sharply in passing through matter. This is proof that an alpha particle occasionally encounters something that is able to turn it from its course. By analogy, if rifle bullets, fired off at random in a forest, have distances of free flight much greater than the average distance from tree to tree, we may conclude that the bullets ordinarily pass right through a tree without interference. If we found an occasional bullet to be sharply deflected, we might infer that each tree or an occasional tree contained something—perhaps a slender rod of heartwood—which was tough enough to deflect any bullet that happened to encounter it.

What, then, is the nature of that impenetrable something, within the atom, which is able to deflect an occasional alpha particle from its course? Since the alpha particle itself is positively charged, it seems reasonable to think that it may be deflected by being repelled by something else that is positively charged. In other words, we assume that within every atom there is a positively charged *atomic nucleus*, which is very small in comparison with the atom as a whole. When a speeding alpha particle strikes an atom it usually passes right through; but if it happens to pass very close to the nucleus of the atom it is repelled by the positive charge on the nucleus, and deflected from its course.

► 230. Atoms as Solar Systems

All atoms, then, contain positive electricity, concentrated in the nucleus. But they all must contain negative electricity (electrons) as well, as is evidenced by the emission of electrons by metals or even by non-metals, at sufficiently high temperatures or under the influence of radiant energy of sufficiently high frequency. From the ease with which many atoms lose electrons we are inclined to believe that the electrons are in the outer part of the atom and the positively charged nucleus at its center.

Since matter, as ordinarily encountered, is electrically neutral, it is plain that *an atom ordinarily possesses as many electrons in the outer part of the atom as it has positive charges on its nucleus*, thus making the atom as a whole electrically neutral. Since an electron is of negligible mass and since no atom (as we shall presently see) contains more than 96 electrons, it is plain that *most of the mass of every atom is in its positively charged nucleus.*

We may assume that the electrons in an atom revolve about the nucleus with sufficient velocities to keep them from being drawn into the nucleus by the attraction of the positive charge of the nucleus. The space between the nucleus and the electrons is presumed to be just empty space, penetrable by an alpha particle or by any other swiftly moving projectile of sufficiently small size.

Only occasional alpha particles (traced by fog tracks) are sharply deflected, after traversing perhaps two hundred thousand atoms. It is therefore concluded that the nucleus of an atom is very small. Its diameter compares with that of the atom as a whole about as the diameter of the sun compares with that of the solar system.

To summarize: Atoms are often represented as being somewhat like miniature solar systems, each with a heavy, positively charged nucleus of extremely small size, about which electrons whirl, at considerable distances from the nucleus. This view of the internal architecture of atoms originated with the British physicist *Rutherford,* in 1911.

► 231. The Charge on the Nucleus

Rutherford's view of atomic structure left important details to be worked out. For example, how great is the charge on the nucleus of an atom of any particular kind? What determines the mass of the atom? How many electrons are there in any particular kind of atom, and how are they arranged?

It was soon observed that when alpha particles are made to pass through thin sheets of metals they are the more strongly deflected

from their original paths the nearer these metals are to the end of the Periodic Table. So it was plain that the charge on the nucleus of an atom must *increase* as we pass forward through the table. The simplest assumption is that it increases by one unit with each step through the table. Since an atom is normally electrically neutral *the number of electrons that revolve in orbits about the nucleus must be equal to the number of positive charges on the nucleus,* and must likewise increase by one for each step forward through the table. The experiments of Moseley (§ 216) confirmed this supposition. For any given

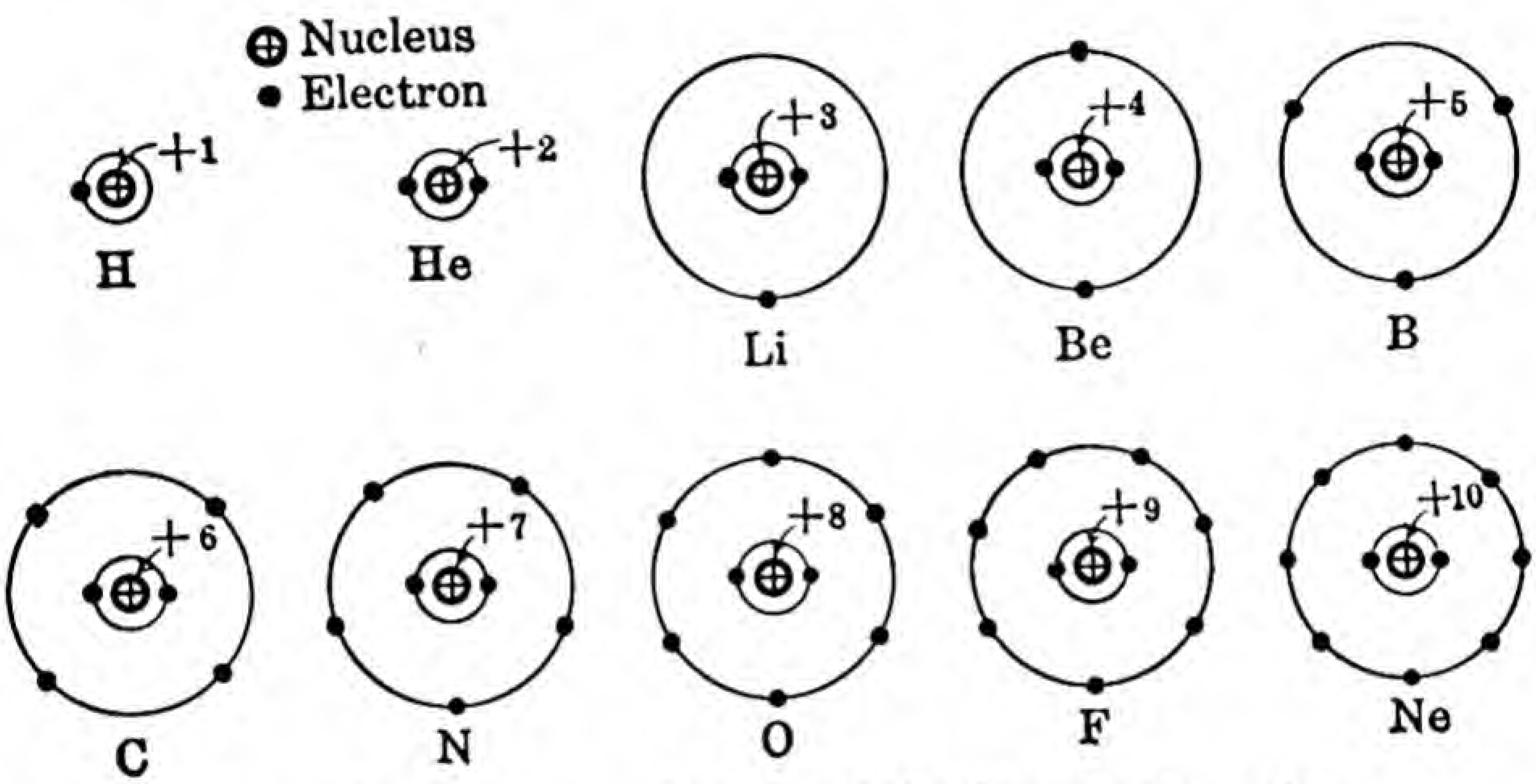


FIG. 95. Structure of atoms of the first ten elements.

element, the charge on the nucleus and the number of electrons outside the nucleus are both given by the *atomic number.*

Figure 95 shows the structure of the atoms of the first ten elements, according to this view. An atom of hydrogen contains a positively charged nucleus, of unit weight, called a *proton,* which we have previously been representing by the symbol H^+. Outside this nucleus, in a neutral hydrogen atom, H, is a single electron, rotating in a circular or elliptical orbit. Then, as we pass forward through the Periodic Table, from hydrogen toward uranium, each step adds 1 unit of positive charge (and, ordinarily, some additional mass) to the nucleus, and 1 more electron to the total number of electrons. (Ex. 1.)

232. Accounting for Isotopes

It seems probable that the nucleus of every atom consists of *protons* (particles of unit positive charge and very nearly unit mass),[2]

[2] On the scale that makes an atom of the most abundant isotope of oxygen weigh 16 units.

and *neutrons* (particles of zero charge and very nearly unit mass). There must be enough protons in the nucleus of every atom to account for its charge, which is given by the atomic number of the element and is the same for all the isotopes of the element. These protons will have a certain total mass; then enough neutrons must be present to account for the rest of the mass of the nucleus (which is very nearly the mass of the atom as a whole, since the electrons surrounding the nucleus are of very nearly negligible mass).

For example, the two isotopes of chlorine (atomic number, 17) are of masses 35 and 37, hence are often represented as $^{35}_{17}Cl$ and $^{37}_{17}Cl$. (Observe that the lower figure in such symbols indicates the atomic number and nuclear charge, whereas the upper figure indicates the isotopic mass.) We account for the nuclear charge of 17 (also for 17 units of mass) by assuming that each of the chlorine isotopes contains 17 protons in the nucleus, together with enough neutrons to make up the remaining mass. So the nucleus of $^{35}_{17}Cl$ probably consists of 17 protons and 18 neutrons, and the nucleus of $^{37}_{17}Cl$ consists of 17 protons and 20 neutrons. (Ex. 2, 3.)

► 233. Accounting for Periodic Properties

Now let us attempt to account for periodic properties:

1. There are reasons for believing that an atom is able to influence its neighbors or enter into chemical union with them because of electrical or electromagnetic forces which it exerts upon neighboring atoms.

2. Obviously, the *outermost* electrons in any one atom are the ones which approach most closely to neighboring atoms and hence exert the strongest forces upon neighboring atoms.

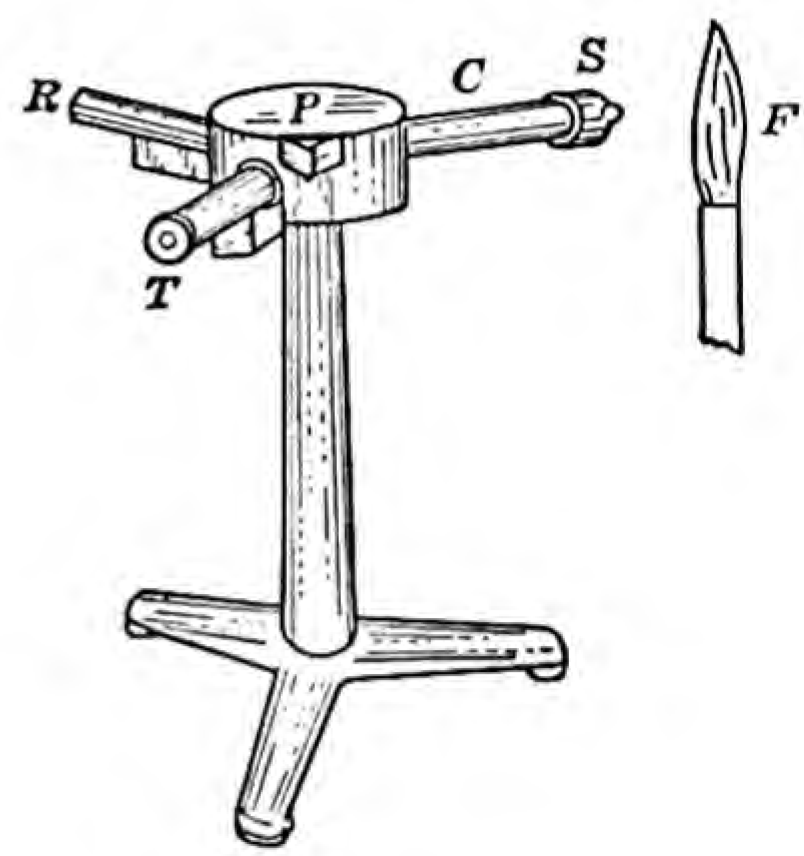
3. So the repeated recurrence of *chemically similar elements*, as we pass forward through the periodic table, must be due to the repeated recurrence of *similar groups of electrons in the outermost part of the atom*. The elements in any one column of the Periodic Table nearly always possess the same grouping or arrangement of electrons in the outer part of the atom. (Ex. 4.)

► 234. Electron Orbits

The groupings of electrons that exist within the atoms of any given element are revealed by the character of the light emitted when the element is heated to a high temperature in a flame or an electric arc.

The various colors composing the light may be sorted out by the prism of a *spectroscope* (Fig. 96), and then appear as separate colored lines [3] or bands in what is called the visible *spectrum* of the element [4]; or they may be registered on a photographic plate, along with certain lines that represent radiant energy in the ultraviolet or infrared regions, invisible to the eye.

We think of individual atoms, introduced into a flame or an electric arc, as accepting energy, which serves to remove one or more electrons in each atom from orbits near the nucleus to new orbits, farther



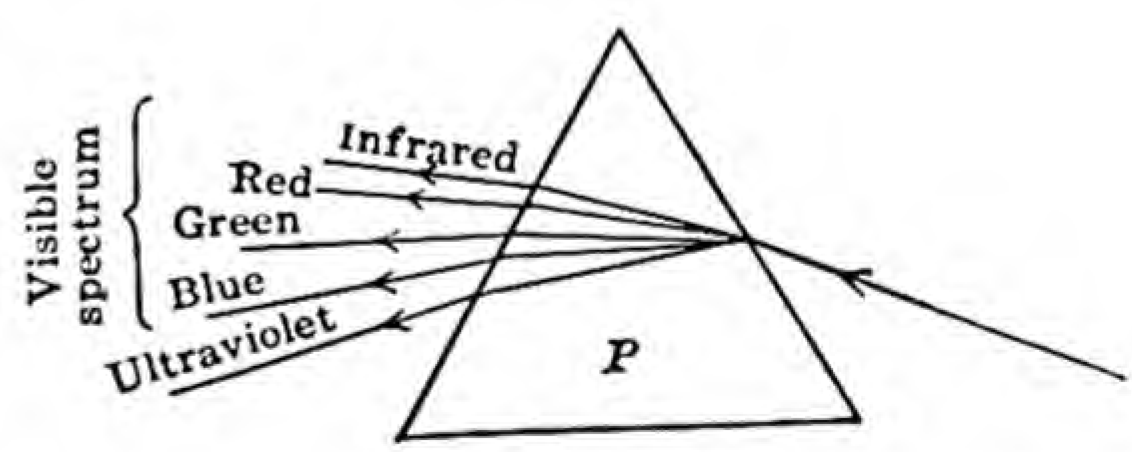


FIG. 96. A spectroscope. The tube *C* contains lenses that render the light rays parallel. The prism *P* bends the path of the light through an angle, which is greatest for the ultraviolet and least for the infrared. As the telescope *T* is swung through an arc the different lines of the spectrum of the element examined appear successively in the field of the telescope. *R* contains a comparison scale that may be reflected from the prism, as an aid in identifying the different lines of the spectrum.

from the nucleus. A physicist would express this by saying that the electrons are raised from their normal or customary *energy levels* to higher energy levels.

But a removed electron occupies its new orbit only momentarily. It almost instantly reverts or "falls back" to another orbit, nearer the nucleus (regaining its original, stable orbit in one or more steps). In doing so it releases energy, which goes flying off through space as a pulse of radiant energy, which is recorded as a definite line in the spectrum of that element.

[3] Each line is in reality a magnified image of the narrow slit through which light is admitted to the spectroscope.

[4] Provided that the electron concerned is one in the outer part of the atom. The disturbance of an electron near the nucleus usually results in a line in the X-ray spectrum, when the disturbed electron reverts to its original orbit.

► 235. The Bohr Theory

In 1913 the Danish physicist Bohr assumed that the electrons within an atom may possess certain definite orbits and no others. On passing over or falling in from one definite orbit to another a definite amount of radiant energy is released, which is registered as a definite line in the visible spectrum of the element.[3]

By listing and comparing the *frequencies* (footnote, p. 266) corresponding to the numerous lines in the spectrum of each element, information has been gained about the grouping of electrons within each type of atom. It turns out to be as shown in the Periodic Table on p. 255, or facing the back cover of this book. The letters *K*, *L*, *M*, etc., appearing in the table in connection with each element, are arbitrary designations for successive groups of electrons within the atom, counting outward from the innermost, or *K*, group. (Ex. 5, 6.)

Turn to the table and notice, first, that *with the exception of palladium no atom is ever found to contain more than 8 electrons in its outermost group of electrons.* In other words, a group of electrons is ordinarily not built up beyond 8 until a new group, farther from the nucleus, has been begun. Examples, from the second row of the Periodic Table

	Li	Be	B	C	N	O	F	Ne
K group:	2	2	2	2	2	2	2	2
L group:	1	2	3	4	5	6	7	8
Total number of electrons (atomic number):	3	4	5	6	7	8	9	10

Observe, furthermore, that the number of electrons necessary to complete any given group, from the *K* group, outwards, is 2, 8, 18, 32. This is obviously the reason why 2, 8, 18, or 32 elements are needed to complete a row in the Periodic Table. Numbers of electrons are given in the table in bold-faced type when the given electron group is complete. (Ex. 7.)

The *transition elements* in the Periodic Table are those which have at least one incomplete group of electrons, within the outermost group. The post-transition elements are those which have only the outermost group incomplete. (Ex. 8, 9.)

236. Wave Mechanics

The Bohr theory has now been superseded by a mathematical interpretation of atomic structure termed *wave mechanics*, which Bohr himself assisted in developing. It still views every atom as consisting of a massive, positively charged central nucleus and a number of

electrons equal to the atomic number of the element. It distributes the electrons into the very groups and subgroups that were recognized by the Bohr theory.

The chief novelty of wave mechanics is that *the electron is no longer regarded as a particle*, but as something having the nature of a wave, controlled by mathematical equations. These no longer limit the electrons to definite orbits, though the most probable location for any electron at any given moment is in one of the Bohr orbits or in its immediate neighborhood. The internal structure of the atom has gained in precision by becoming a branch of advanced mathematics, but has lost in vividness. It seems impossible to sketch or diagram what ordinary language may perhaps describe as "a massive positively charged something, surrounded by a pulsating halo or series of concentric halos of negative electricity." So there is little value in the once-popular diagrams in which electrons were made to appear as particles, revolving in definite orbits.

► 237. Why the Inert Gases Are Inert

In Fig. 97 is a curve giving the *ionization potential* for nearly every element. This is a measure of the *energy* that is required to remove an electron from an atom of the element, thus converting the atom into

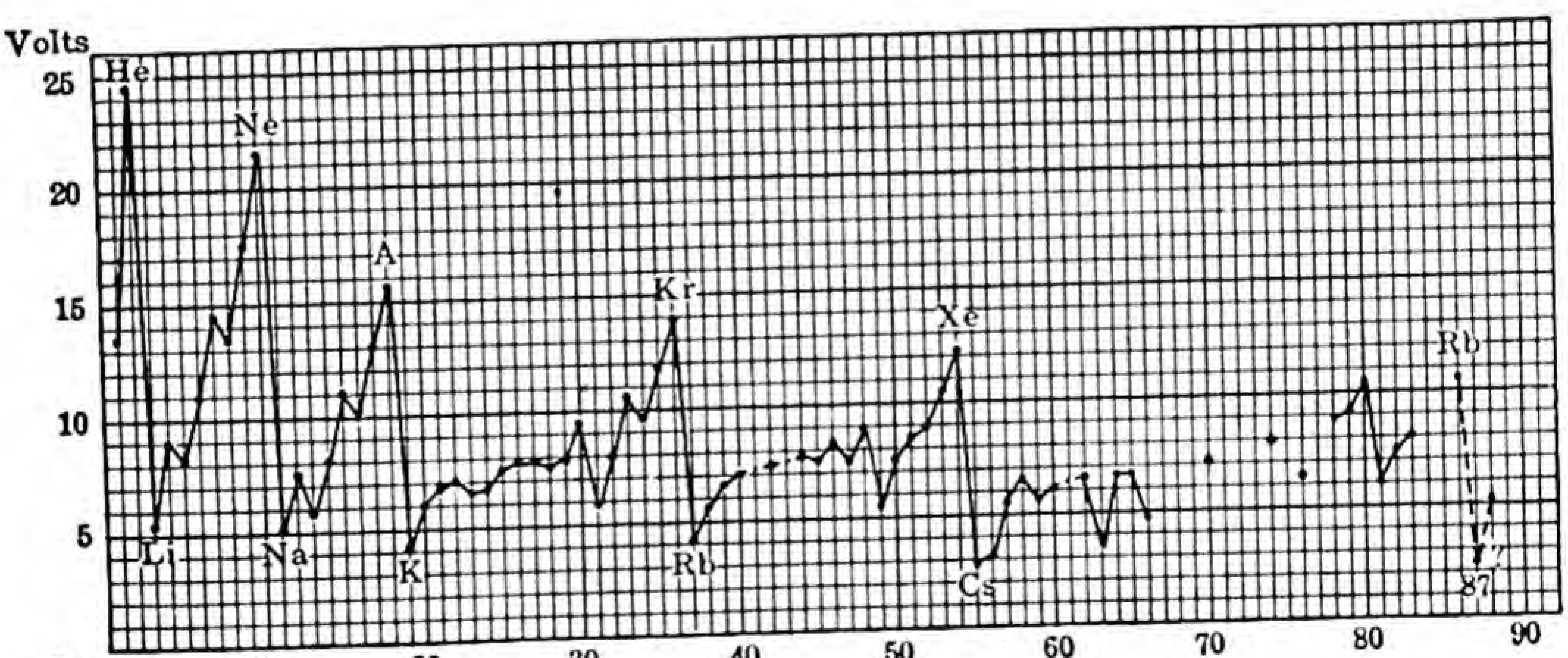


FIG. 97. Ionization potentials.

a singly positively charged ion. We notice from this curve that *the ionization potentials of the inert gases are higher than for neighboring elements*. This bears witness that *the group of two electrons possessed by the helium atom, and the outer octet or group of eight electrons possessed by every other inert-gas atom, is a stable group, disrupted with considerable difficulty.*

The electrons of the *octet* (stable group of eight electrons, possessed by all the inert gases except helium) are paired. One electron of each pair spins in the opposite direction to the other, hence the electromagnetic force that it exerts offsets that of the other. So, the total electrical or electromagnetic force which the octet is able to exert on other atoms is very nearly zero. That is why atoms of the inert gases fail to enter into chemical union with other elements or with one another, and even fail to combine in pairs (as do atoms of other elements in H_2, O_2, N_2, etc.). It also explains why the inert gases are difficult to liquefy.

► 238. The Metals

The next step beyond each inert gas, in passing through the Periodic Table, gives us an *alkali metal*, in column 1A of the table, with a single electron in the outermost shell of electrons. Figure 97 shows a sudden *decrease* of the ionization potential (from 21.47 volts, for neon, to 5.12 volts for sodium). It is evident that the one electron which is found in the highest energy level or outermost shell of an atom of an alkali metal is always easily removed.

Comparing the alkali metals with one another, we find that the ionization potential decreases in the order Li, Na, K, Rb, Cs (that is, with an increase in the number of shells of electrons). There need be no mystery in this: *The more shells of electrons there are, the farther from the nucleus the outlying single electron must be, and the less strongly it will be held by the attraction of the positive charge on the nucleus.*

With the *alkaline-earth metals* we have two electrons in the outermost shell. The first of these is readily removed. Thus we obtain a singly positively charged ion, such as Ca^+. This, on account of its surplus positive charge, retains its remaining electrons more strongly. Nevertheless a second electron may ordinarily be removed, giving a doubly positively charged ion, such as Ca^{++}.

To go further and remove a second electron from an alkali-metal atom, or a third electron from an alkaline-earth atom, demands the expenditure of much more energy than was required to remove either of the first two electrons. We are thus confirmed in our previous conclusion, based on spectral data (§ 234), *i.e.*, that the second electron in the atom of an alkali-metal or the third electron in an alkaline-earth atom belongs to a lower energy level.

When atoms of the alkali metals lose one electron each, or when those of the alkaline-earth metals lose two electrons each, as just described, ions

are produced that have the stable pair or stable octet characteristic of the inert gas that next precedes the given metal in the Periodic Table:

	Metallic Atom		*Metallic Ion*	*Preceding Inert Gas Atom*
	K	$-\,e \rightarrow$	K^+	A
Charge on nucleus	19		19	18
Electron groups	2, 8, 8, 1		2, 8, 8	2, 8, 8
Net charge	0		+ 1	0
	Ca	$-\,2e \rightarrow$	Ca^{++}	A
Charge on nucleus	20		20	18
Electron groups	2, 8, 8, 2		2, 8, 8	2, 8, 8
Net charge	0		+ 2	0

Observe that these ions resemble atoms of the preceding inert gas only in their *electronic* structure. They differ from inert gas atoms in having *a higher positive charge on the nucleus,* hence possess a net positive charge, instead of being electrically neutral. (Ex. 10.)

It is very probable that no metallic atom ever loses more than two electrons in forming a simple metallic ion. Such apparent exceptions as the ferric ion, Fe^{+++}, and the stannic ion, Sn^{++++}, probably do not really exist as simple ions, but are always linked to other atoms or ions, to form complex ions or neutral molecules. Details will appear in the next chapter (§ 244). (Ex. 11.)

► 239. The Non-Metals

Non-metallic atoms contain from four to seven *valence electrons* (a name given to electrons in the outermost group of the atom). They can attain a stable group of eight electrons (like that of the *next following* inert gas) by *gaining* electrons from an outside source. Thus the halogens (Column 7A of the Periodic Table) each possess seven valence electrons, and tend to acquire one more, thus forming negatively charged halide ions, which possess an octet:

$$\underset{\text{Seven valence electrons}}{Cl} + e \rightarrow \underset{\text{Eight valence electrons}}{Cl^-}$$

Members of the oxygen family (Column 6A of the Periodic Table) similarly tend to gain two electrons, thus producing a doubly negatively charged ion, with an octet:

$$\underset{\text{Six valence electrons}}{S} + 2e \rightarrow \underset{\text{Eight valence electrons}}{S^{--}}$$

If only one or two electrons are thus gained the process actually *releases* energy. The non-metal is then often said to possess *electron affinity.*

When more than two electrons are needed to complete an octet for a non-metallic atom, the process *demands* energy instead of releasing energy. Ordinarily a sufficient supply of energy is not available; hence non-metallic atoms that need more than two electrons to complete their octet (*e.g.*, nitrogen, phosphorus, carbon, and silicon) do not ordinarily gain electrons, to form negatively charged ions (C^{----}, for example). Instead, they complete their octets by combining with other atoms, as described in the next chapter.

The non-metals may be arranged in the order of decreasing tendency to gain electrons, in forming negative ions. This is the order of *decreasing electronegative character* or *decreasing non-metallic character.* The halogens would head such a list; and fluorine is the most electronegative of all the halogens, for the simple reason that its electrons are all very close to the positive charge on the nucleus, and hence are very strongly attracted. (Ex. 12, 13.)

240. Summary

Our views with regard to the internal architecture of atoms were not obtained by lucky guess, revelation, or sudden inspiration. They are the result of laborious observation of a multitude of facts, dealing with the phenomena of radioactivity, details about valence, the amazingly complicated details of spectra, and an imposing array of electrical phenomena. Guided by these facts, our present ideas gradually took form, during a period of about thirty years, through the efforts of Rutherford, Bohr, and later workers.

To learn only the final conclusion, namely, that every atom contains a heavy positively charged nucleus, about which electrons whirl in one or more energy levels, is to miss the purpose and spirit of our discussion. The important thing is to understand and remember the *reasoning* that led to this conclusion.

How do we know that atoms are penetrable? How do we know that there is a positively charged nucleus, and that most of the mass of the atom is there? How has the charge on the nucleus been determined? What leads us to believe that the nucleus is composed of protons and neutrons? How do we know that the nuclear charge is also the number of electrons? To know and understand the answers to these questions is more than a feat of memory. It calls for imagination and intelligence. (Ex. 14–16.)

Technical Words

Phosphorescent, p. 263. **Electroscope,** p. 264. **Spectroscope,** p. 273.

Radioactivity—continuous emission of invisible rays, which affect a photographic plate, discharge an electroscope, and leave visible fog tracks in moist air.

Atomic energy—energy stored in any manner within the nucleus of an atom.

Alpha, beta, gamma rays, p. 266.

Radiant energy, p. 266 (footnote). **Frequency,** p. 266 (footnote).

Spectrum (plural, **spectra**)—an image formed when a beam of radiant energy is separated into its component frequencies, by being passed through a *prism* or by being reflected from a *grating*. The different components of the original beam are then registered on a photographic plate or are otherwise observed in the order of increasing or decreasing frequency.

Grating or diffraction grating—a series of closely ruled, parallel lines on a flat surface, having the property of reflecting light in such a manner as to separate the different frequencies.

Proton, p. 271. **Neutron,** p. 272. **Valence electron,** p. 277.

Ionization potential—the potential, in volts, that must be applied to remove a specified number of electrons from a neutral atom.

Exercises

1. From the position of iron in the Periodic Table infer the charge on the nucleus of the iron atom and the number of electrons surrounding the nucleus.
2. Account for three isotopes of magnesium of isotopic weights 24, 25, 26.
3. What symbols represent the three different isotopes of hydrogen (§ 96)? What is the probable structure of an atom of each?
4. What other elements possess the same external group of electrons as neon? What name is given this family of elements?
5. Refer to the Periodic Table to determine how many electrons in each group of an atom of argon and an atom of iron.
6. Examine the table to determine whether metals usually have a large or a small number of electrons in the outermost group, as compared with non-metals.
7. With which element is the K group completed? The L group? The M group? The N group?
8. Which of the inert gases does not have an outer octet of electrons?
9. What are the atomic numbers of the transition elements in the period of the Periodic Table that includes iron? Which two groups of electrons in these elements are incomplete? With what element does the innermost of these two groups become complete?
10. The barium ion, Ba^{++}, has the same electronic structure as which inert gas atom? In what respect do these two particles differ?
11. Would you expect element 87 to ionize more or less readily than the other alkali metals? Why?
12. Which of the elements in Column 6A of the Periodic Table is most electronegative?
13. Show that an alpha particle is really a helium nucleus.

14. Why is it assumed (*a*) that atoms are penetrable, (*b*) that every atom has a positively charged nucleus, (*c*) that electrons are present in a number equal to the charge on the nucleus, (*d*) that electrons rotate about the nucleus?

15. In what two ways has the charge on the nucleus been measured, at least roughly?

16. Describe an electroscope and explain how it is used.

Chapter 19

BUILDING MOLECULES

241. What Holds Atoms Together, in Forming Molecules?

Our everyday chemical formulas bear witness that we know how many atoms of each kind are combined in forming any given kind of molecules. This still leaves us wondering just how atoms manage to lay hold of one another in chemical union. For a long time chemists let this fundamental question pass by saying that combining atoms possess *affinity* for one another. That, of course, explained nothing. They might as well have said that atoms combine from a sense of duty or force of habit.

The Swedish chemist Berzelius (1819) guessed that atoms may be held together by electrical forces, certain atoms being positively and others negatively charged. He assigned positive charges to atoms of hydrogen and the metals, since these move toward the negatively charged electrode (cathode) and are there separated as hydrogen gas or in metallic form, when a current passes through a solution. To non-metallic atoms Berzelius assigned negative charges. If hydrogen atoms are positively charged and oxygen atoms negatively charged, these oppositely charged particles should attract each other, and perhaps cling together, to form molecules of water. Similarly for other compounds.

The views of Berzelius encountered difficulties in explaining why a given set of elements usually combine in several different proportions, to form a corresponding number of related compounds (§ 169). Furthermore, when it was proved that a molecule of oxygen (for example) contained two atoms, it was hard to imagine why two atoms, *both* negatively charged, should combine with each other. Again, if only oppositely charged atoms combine, it seemed difficult to explain how negatively charged atoms of chlorine could be *substituted* for positively charged atoms of hydrogen, atom for atom, in the molecules of numerous compounds of carbon (§ 202), as was definitely proved to be true in 1834.

The conclusion ultimately was reached that *atoms are really drawn toward one another and held together by forces set up by the electrical charges carried by the atoms; but every atom normally carries both positive and negative charges, in equal amounts.* Further progress had to await the discovery of the electron and a knowledge of some of the details of the internal structure of atoms, as related in preceding chapters. Let us consider, first, *ionic compounds*, in which the positively and negatively charged parts of the compound exist as nearly independent substances, subject only to the condition that the material as a whole shall be electrically neutral.

► 242. Ionic Compounds

We have learned (§ 238) that it is easy for an atom of an alkali metal to lose one electron, or for an atom of an alkaline-earth metal to lose two electrons, thus forming a positively charged ion. This process *demands energy.*

An atom of any of the most pronounced non-metallic elements, on the contrary, possesses a tendency to combine with one or two electrons, thus forming a negatively charged ion (§ 239). Frequently this process *releases energy.* It is sometimes aided by two other processes that release energy: (1) *crystal formation* (in which the oppositely charged ions approach one another, with consequent decrease in potential energy, in taking up their positions in the space-lattice of a crystal); (2) the process of hydrating the ions, in dissolving the crystal in water.

With the most pronounced metals the formation of a univalent or divalent cation ordinarily demands no more energy than the formation of an anion is able to supply, when supplemented by energy released in crystal formation. It is therefore not surprising that *the most pronounced metals cannot exist as uncharged atoms in the presence of the most pronounced non-metals*, but transfer electrons to the non-metals, thus forming *ions*, which are present even in the crystal (§ 142). Examples: $NaCl$, $MgCl_2$, KBr, MgO, CaS. These are typical *ionic compounds.* (Ex. 1, 2.)

► 243. Accounting for Hydrogen Chloride Gas

Since the single electron in a hydrogen atom is relatively close to the nucleus it is strongly attracted by the positive charge on the nucleus, hence much more energy is needed to remove it than to remove an electron from an atom of lithium or sodium. In transferring this electron to an atom of chlorine, energy would be released, but *not much more than a third of what the first process demands.*

Accordingly, a compromise is made. The hydrogen *partially* transfers its electron to a neighboring chlorine atom, retaining it still within its own sphere of attraction; and in return accepts a share of control over one of the valence electrons of the chlorine atom. So we obtain a stable new system, in which two electrons are permanently shared between the hydrogen and chlorine atom, linking them together, thus forming a molecule of hydrogen chloride gas, $H\overset{\cdot}{\underset{\times}{}}\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$. The small cross here represents the single electron that originally belonged to the hydrogen atom, and the seven dots represent the seven valence electrons that originally belonged to the chlorine atom (neglecting electrons in two inner shells of the chlorine atom).

If we count the pair of shared electrons as belonging to the hydrogen atom, then this has the stable *pair* of the electrons that is characteristic of the inert gas *helium;* but if we count them as belonging to the chlorine atom, then this has the stable outer *octet* that is characteristic of the inert gas *argon.* Atoms linked together by pairs of shared electrons are said to possess *covalent linkage.* (Ex. 3.)

244. When to Expect Covalent Linkage and How to Recognize It

The alert reader here interrupts to ask how anyone can know whether any given compound is composed of separate ions, or whether its atoms are linked in covalent union, as just described. The answer has already been suggested: In removing only *one* or *two* electrons from a metallic atom of reasonably large radius the energy expended (work performed) in overcoming the attraction of the nucleus for the electrons being removed is never very great. It is usually offset by energy released in forming the anion (supplemented by energy released in crystal building or in hydrating the ions). In consequence, the ions are actually produced.

To remove three or four electrons from an atom (to form Al^{+++} or Sn^{++++}, for example) much more energy is required than to remove but one or two, since each additional electron needs to be removed in spite of the attraction of an increased positive charge on the ion that remains. Indeed, when the cation that would be formed is of unusually small radius (H^+, Be^{++}) or of higher charge than $+2$, its formation demands more energy than can be supplied by the formation of the anion, supplemented by crystal building or hydration. In consequence, complete transfer of electrons, with formation of ions, fails to take place; instead, electrons are *partially transferred,* thus producing

covalent linkage. *Simple cations of higher charge than +2 are rarely formed;* or it may happen that a part of the material will be ionized, in equilibrium with a part in the covalent condition.

The principle just stated is illustrated by the following table. We have learned (§§ 142, 143) that ionic crystals possess (1) *high melting points* and (2) *high boiling points.* Moreover, (3) ionic crystals melt to form liquids that are good conductors of electricity. By these tests the chlorides on the left of the broken line are plainly *ionic*, and those on the right are plainly *non-ionic*, namely, covalent. Only beryllium chloride, $BeCl_2$, is doubtful, forming a few ions when melted, though still existing chiefly as uncharged molecules. (Ex. 4, 5.)

Properties of Some Metallic Chlorides

Λ = formular conductance (§ 519) of the fused salt.

	HCl		
m.p.	−114°		
b.p.	−85°		
Λ	10^{-6}		
	$LiCl$	$BeCl_2$	BCl_3
m.p.	606°	404	−107°
b.p.	1337°	(500°)	12.6°
Λ	166	0.066	0
	$NaCl$	$MgCl_2$	Al_2Cl_6
m.p.	800°	718°	190° (2.5 atm)
b.p.	1442°	(1000°)	183° (sublimes)
Λ	134	29	15×10^{-6}
	KCl	$CaCl_2$	$GaCl_3$
m.p.	768°	774°	75.5°
b.p.	1415°	(1100°)	205°
Λ	104	52	10^{-7}
	$RbCl$	$SrCl_2$	$InCl_3$
m.p.	717°	870°	586°
b.p.	1388°	(1250°)	(550°?)
Λ	78	56	14.7
	$CsCl$	$BaCl_2$	$TlCl_3$
m.p.	645°	960°	ca. 25°
b.p.	1289°	(1350°)	(100°)
Λ	67	65	10^{-3}

IONIC COVALENT

We have already noticed (§ 186) that, though gaseous hydrogen chloride is a covalent compound, we obtain an ionic compound, hydrochloric acid, by dissolving the gas in water. The water brings new forces into action, which result in the removal of a proton, H^+, from the hydrogen chloride molecule and its transfer to the water:

$$H_2O + HCl \rightarrow \underbrace{H_3O^+ + Cl^-}_{\text{Hydrochloric acid}}$$

The extra energy needed for separating the H^+ from the Cl^- is supplied by the hydration of the ions (direct union of the proton and of the chloride ion with water). The other covalent chlorides, such as Al_2Cl_6 or PCl_3 (§ 277), usually also react with water, though in a somewhat different way. (Ex. 6.)

► 245. Accounting for Ammonia Gas and the Ammonium Ion

As another example of electron sharing consider the direct union of nitrogen gas with hydrogen (in the presence of a catalyst) to form ammonia, $\begin{matrix} & H & \\ & \times\cdot & \\ H\,{}^{\cdot}_{\times} & N & : \\ & \cdot\times & \\ & H & \end{matrix}$. The three crosses represent electrons that originally belonged to the three hydrogen atoms. The five dots represent the five valence electrons of the nitrogen atom (neglecting the inner pair of electrons, next the nucleus). We observe that three pairs of electrons, in the completed molecule, are shared between nitrogen and hydrogen, and that one electron in each pair was furnished by a hydrogen atom and one by the nitrogen atom. If we consider the shared electrons as belonging to the hydrogen atoms, then each of these has the stable electron pair that is characteristic of the inert gas *helium;* if we consider the shared electrons as belonging to the nitrogen atom, then this has the stable outer octet that is characteristic of *neon.*

If we ask why nitrogen does not share all five of its valence electrons with hydrogen atoms, thus forming NH_5, one might be tempted to answer that this would give nitrogen an unstable outer group of ten electrons instead of a stable octet. But the octet idea fails to predict many compounds that actually exist. A better answer is to note that *as each new hydrogen atom attaches itself to the nitrogen atom the potential energy of the system decreases, but reaches a minimum with* NH_3 (thereafter increasing because of the tendency of the hydrogen atoms to repel one another).

But a proton, H^+, in contrast with an uncharged atom of hydrogen, H, is negligibly small, and its positive charge causes it to be strongly attracted by the outlying electrons in the ammonia molecule, $\begin{array}{c}\mathrm{H}\\ \mathrm{H}:\ddot{\underset{\cdot\cdot}{\mathrm{N}}}:\\ \mathrm{H}\end{array}$.

The ammonia molecule therefore can bind the proton fast, by a pair of shared electrons. Thus we account for the *ammonium ion*,

$$\left[\begin{array}{c}\mathrm{H}\\ \mathrm{H}:\ddot{\underset{\cdot\cdot}{\mathrm{N}}}:\mathrm{H}\\ \mathrm{H}\end{array}\right]^+.$$

We have bracketed this formula, to indicate that *the positive charge brought into the molecule by the proton belongs to the ammonium ion as a whole, and not to any particular atom in it.* Moreover, we here ceased to distinguish between electrons originally furnished by hydrogen atoms and those originally furnished by the nitrogen. The two electrons forming any pair of shared electrons, though furnished by different atoms, are really indistinguishable. We use dots and crosses to distinguish them only when we wish to emphasize how many valence electrons were originally possessed by each of the combining atoms. (Ex. 7.)

246. Character of the Covalent Bond

The **covalence** of an atom is the number of pairs of electrons that it shares with other atoms. *In ordinary covalent union one electron in each pair of electrons originally belonged to each of the two atoms thus linked together.* Thus the covalence of hydrogen is 1, and that of chlorine is 1, in hydrogen chloride; that of nitrogen is 3 in NH_3 and 4 in NH_4^+ (but observe that the *valence number* (§ 171) of nitrogen in NH_3 and NH_4^+, is -3). Covalence, unlike ionic valence, is never given a + or − sign.

What actually happens when a pair of electrons forms a covalent link? One detail we know: *The electrons forming the bond always spin in opposite directions.* But oppositely spinning electric charges set up an electromagnetic force, which draws them toward each other. Since the spinning electrons belong to or are under the influence of two different nuclei they drag these nuclei after them as they approach each other. Thus the two nuclei become linked.

The actual motions or orbits of the shared electrons are still unknown. Computations based on wave mechanics merely inform us that *the shared electrons circulate about both nuclei, but are most likely*

to be found, or spend most of their time, in the region between them. By contrast, two electrons spinning in the same direction would spend less of their time between the two atoms than elsewhere.

The final distribution of the electrons, and the center-to-center distance between the bonded atoms, are those that give the completed molecule minimum potential energy. In a few instances, wave mechanics enables us to calculate the potential energy of a system of two particles at different distances of approach. Too close an approach always results in repulsion, owing chiefly to the mutual repulsion of the positively

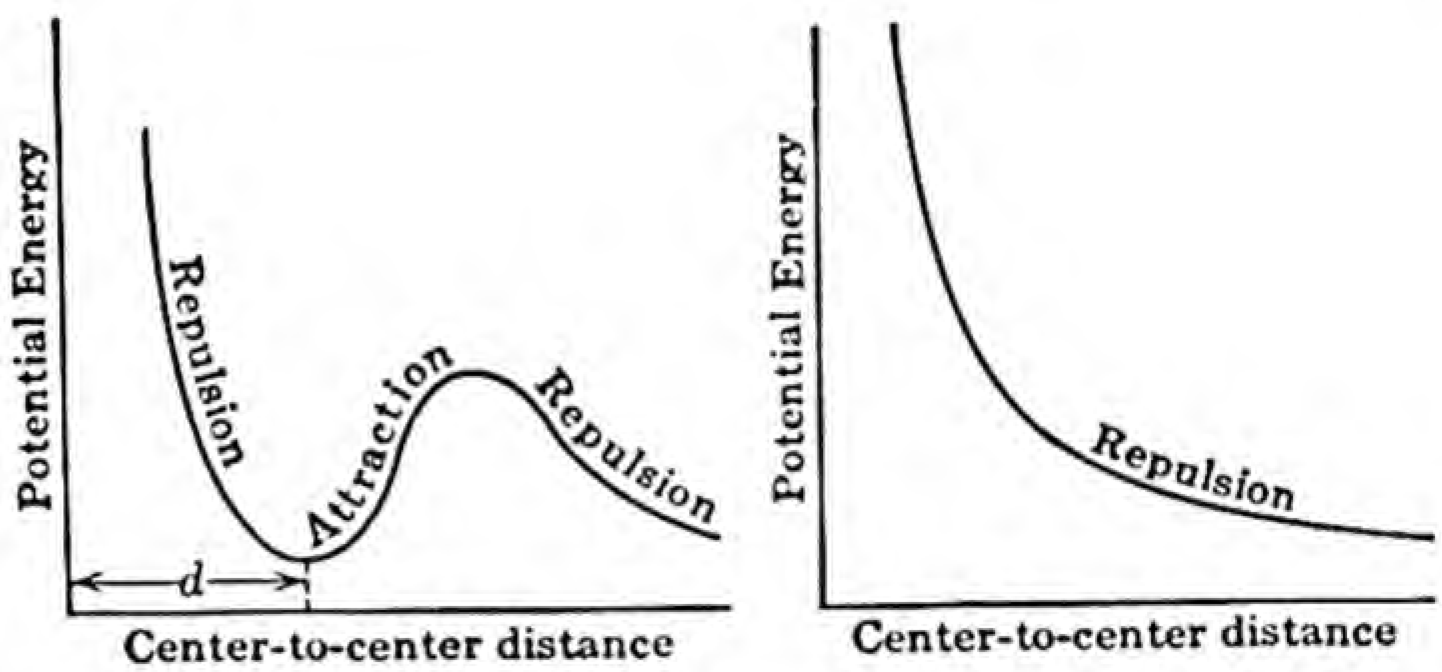


FIG. 98. Showing the potential energy of a pair of atoms, at different distances of approach.

charged nuclei. As the particles separate, under the influence of this force, potential energy diminishes. But presently, at some distance *d* in the left-hand diagram of Fig. 98, repulsion is balanced by attraction, whenever the two particles possess electrons that can be paired in the same energy level to spin in opposite directions. Potential energy is then at a minimum and the two particles become linked, swinging back and forth on either side of the point of minimum potential energy.

Of course it sometimes happens that minimum potential energy is found at so great a distance of separation that the bond between the particles is too feeble to resist being broken by collision with neighboring molecules. Furthermore, when no electrons are paired to spin in opposite directions, repulsion between the two particles continues to indefinite distances of separation, as shown in the right-hand diagram of Fig. 98. There is no position of minimum potential energy, and no linkage is possible.

► 247. Electronic Formulas

In what precedes, we have had a few examples of *electronic formulas*. These indicate the linking of atoms by shared electrons, in forming molecules or ions. As another example, consider two atoms of

chlorine, each with 7 valence electrons. If each atom furnishes 1 electron to form a bonding pair, we have a chlorine molecule, $:\ddot{\underset{..}{\mathrm{Cl}}}:\ddot{\underset{..}{\mathrm{Cl}}}:$. Each of the atoms is here surrounded by a complete octet of electrons, in spite of the fact that there are only 14 electrons altogether—obviously because the pair of shared electrons are counted twice (once for each atom).

An atom of sulfur, by contrast, has only 6 valence electrons, and can acquire an octet only by sharing two pairs of electrons with neighboring atoms. One way of doing this is to form a ring of atoms. Each atom shares a pair of electrons with its next neighbor on the left, and another pair with its next neighbor on the right, as we pass in either direction around the ring. This ring happens to contain 8 atoms, and persists even in crystalline sulfur (§ 304).

Here are some other examples, which the reader should check by making sure that the total number of valence electrons is really the number that would be furnished by the atoms concerned: 1 valence electron for H, 4 for C, 6 for O, and 7 for Cl.

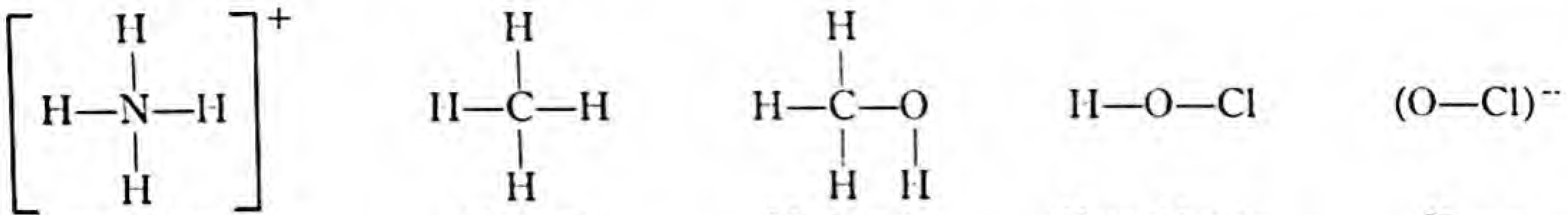
$$\begin{array}{cccccc}
 & & \mathrm{H} & \mathrm{H} & & \\
\mathrm{H:H} & \mathrm{H:}\ddot{\underset{..}{\mathrm{O}}}: & \mathrm{H:}\ddot{\underset{..}{\mathrm{C}}}\mathrm{:H} & \mathrm{H:}\ddot{\underset{..}{\mathrm{C}}}:\ddot{\underset{..}{\mathrm{O}}}: & \mathrm{H:}\ddot{\underset{..}{\mathrm{O}}}:\ddot{\underset{..}{\mathrm{Cl}}}: & \left[:\ddot{\underset{..}{\mathrm{O}}}:\ddot{\underset{..}{\mathrm{Cl}}}:\right]^{-} \\
 & \mathrm{H} & \mathrm{H} & \mathrm{H\ H} & & \\
\text{Hydrogen} & \text{Water} & \text{Methane} & \text{Methanol} & \text{Hypochlorous acid} & \text{Hypochlorite ion}
\end{array}$$

Observe how hypochlorous acid, by losing its proton, H^+, leaves a negatively charged residue, the hypochlorite ion. But this negative charge belongs to the ion as a whole, not to either atom in it; hence we bracket the formula of the ion, then indicate that it carries a unit negative charge (owing to its having 1 extra electron among those shown, as compared with the uncharged atoms). (Ex. 8, 9.)

► 248. Graphic Formulas

Instead of using dots to represent electrons, it is usually more convenient to represent each pair of shared electrons by a stroke or dash, commonly called a *valence bond*. The molecules whose electronic formulas have been given on this and preceding pages are then represented by the following *graphic formulas:*

$$\begin{array}{ccccc}
 & & & \mathrm{H} & \\
 & & & | & \\
\mathrm{H{-}H} & \mathrm{H{-}Cl} & \mathrm{H{-}O} & \mathrm{N} & \mathrm{Cl{-}Cl} \\
 & & & / \quad \backslash & \\
 & & \mathrm{H} & \mathrm{H} \qquad \mathrm{H} & \\
\text{Hydrogen} & \text{Hydrogen chloride} & \text{Water} & \text{Ammonia} & \text{Chlorine}
\end{array}$$



Ammonium ion — Methane — Methanol — Hypochlorous acid — Hypochlorite ion

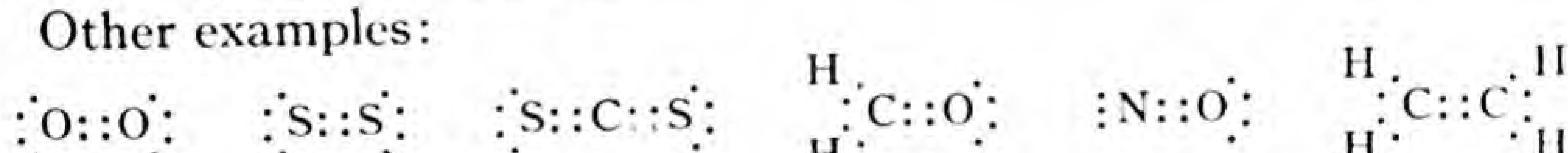
Valence electrons not actually used in linking the atoms together are usually ignored, in writing graphic formulas. (Ex. 10–12.)

Long before electrons were heard of, and long before any distinction was made between ionic valence and covalence, graphic formulas were deduced for thousands of different compounds, through clever interpretation of their chemical reactions. Examples will be given in §§ 453, 454.

► 249. Double and Triple Bonds

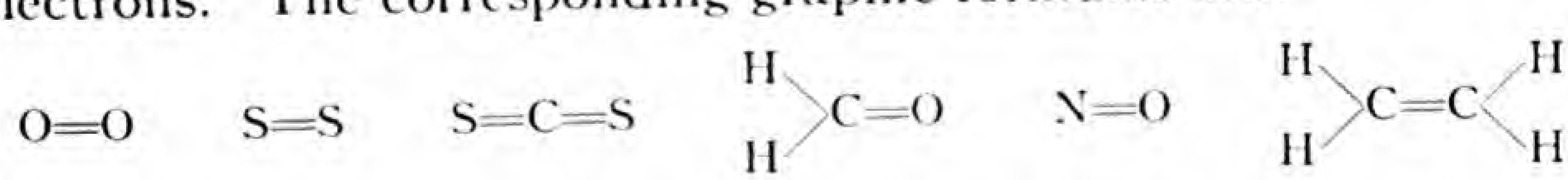
In many instances the only way in which the particles combining to form a molecule can produce a system of minimum potential energy is by having adjacent atoms share more than one pair of electrons. Thus in forming carbon dioxide, CO_2, each carbon atom has 4, and each oxygen atom has 6, valence electrons. Carbon shares two pairs of electrons with each oxygen atom, thus giving a complete octet for each of the three atoms: $\ddot{\underset{\cdot\cdot}{O}}::C::\ddot{\underset{\cdot\cdot}{O}}$. The corresponding graphic formula is O=C=O. Observe the use of *double bonds* here, each representing *two pairs of shared electrons.*

Other examples:



Oxygen — Sulfur vapor — Carbon disulfide — Formaldehyde — Nitric oxide — Ethylene

Observe that each individual atom of carbon, sulfur, or oxygen, by sharing electrons with its neighbors, has acquired a complete octet of electrons. The corresponding graphic formulas are:



We also sometimes encounter *triple bonds*, each representing three pairs of shared electrons:

H—C≡N	N≡C—C≡N	H—C≡C—H
Hydrogen cyanide	Cyanogen	Acetylene

Electronic formulas for these substances would be written:

H:C⋮⋮N: :N⋮⋮C:C⋮⋮N: H:C⋮⋮C:H

It is usually very easy to combine atoms on paper, using double and triple bonds when needed, in such a manner as to secure complete octets. The difficulty is that several different electronic formulas for one and the same substance may often be obtained by this species of "armchair chemistry," all showing the usual covalence of the atoms concerned. And all these formulas may be wrong, since atoms that are large enough may make contact with and often combine with more than four neighboring atoms, and hence become surrounded with more than eight electrons (§ 253). The proper electronic formula to assign to a substance must actually always be settled by determining which of several possible formulas best suggests the chemical reactions or physical properties of the material. We shall learn more about this when we come to study organic compounds, in a later chapter. (Ex. 13, 14.)

The center-to-center distance between atoms depends on the type of bonding, but is rather definite for each type. The radius for atoms of carbon, nitrogen, and oxygen, when singly, doubly, or triply bonded to other atoms, is here given in Ångström units:

C—	0.77	N—	0.70	O—	0.66
C=	0.69	N=	0.63	O=	0.59
C≡	0.61	N≡	0.55		

By adding these radii one may obtain the total center-to-center distance, sometimes called the *bond length*, between the particles thus connected. Thus for C≡N we have $0.61 + 0.55 = 1.16$ Å, fairly accurately, for any compound in which carbon and nitrogen are triply linked. When electron diffraction experiments indicate somewhat different center-to-center distances than are thus calculated, we may conclude that the type of bonding has been somewhat altered, for example, that it is something intermediate between covalent linkage and the ionic state.

The more closely two atoms approach each other, the stronger the bond that unites them and the more work must be expended in breaking the bond and separating them. The table just given shows that a double bond is stronger than a single bond, and that a triple bond is stronger yet. Nevertheless, *when hydrogen or a halogen is directly added to an organic compound it ordinarily adds at the double or triple bond, rather than at any single bond.* The double bond in ethylene (§ 460) accounts for the readiness with which this gas combines directly with chlorine or bromine.

► 250. Coordinate or Semi-Polar Valence

In the pair of electrons forming a *covalent bond*, one electron is derived from each of the two atoms concerned. There is another type of bond, however, in which both the electrons of the pair are furnished by one of the two atoms, the other atom simply acting to accept a share in the pair of electrons. Such a "donated electron pair" constitutes a *coordinate bond* (often called a *semi-polar bond*).

Coordinate bonds are responsible for many familiar and important reactions:

1. We thus account for the *association* of water and many other liquids. Each molecule of water, $\mathrm{H}:\underset{\textstyle\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}}:$ carries two "unshared pairs" of electrons, which it may donate, to form coordinate bonds with the hydrogen atoms of two neighboring molecules. By continuing this process a giant molecule of indefinite dimensions may readily be constructed.

2. In the formation of hydrates, one of the two unused pairs of electrons in the water molecule may be used to link the molecule with an ion. Most cations, in this manner, can combine with four to six water molecules:

$$\left[\begin{array}{ccc} & \mathrm{H} & \\ \mathrm{H} & :\overset{\cdot\cdot}{\mathrm{O}}:\mathrm{H} & \\ \mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}} & :\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{Cu}}}: & \overset{\cdot\cdot}{\mathrm{O}}:\mathrm{H} \\ & \mathrm{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{O}}}: & \overset{\cdot\cdot}{\mathrm{H}} \\ & \mathrm{H} & \end{array}\right]^{++}$$

Tetrahydro-
cupric
ion

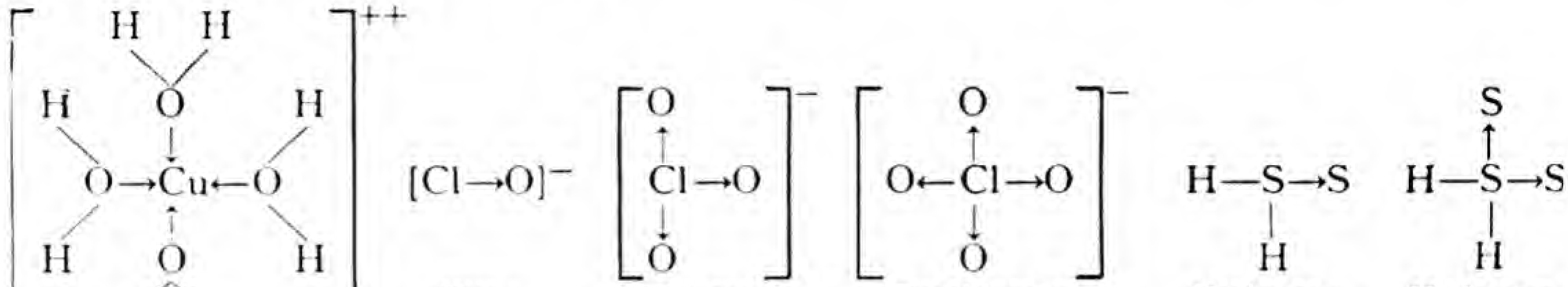
Water in a crystalline hydrate may exist in one or more of four different ways: (1) coordinated with the cation; (2) coordinated with the anion; (3) fitted into the crystal lattice in definite amounts and in a regular pattern, but coordinated with neither ion; (4) entering into open spaces in the lattice in indefinite and variable amounts.

3. Coordinate bonds explain why many molecules and ions, such as Cl^-, and H_2S, though stable enough in themselves, nevertheless may combine with other neutral atoms (such as monatomic oxygen) to form more complex particles: ClO^-, ClO_3^-, ClO_4^-, H_2S_2, H_2S_3.

4. Coordinate bonds also account for *complex ions*, discussed in later chapters (§§ 426, 556, 557).

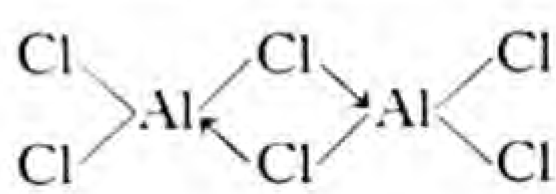
The coordinate bond is often represented by an arrow pointing toward the atom that receives a share in the pair of electrons donated

by the other atom. Thus the ions and neutral molecules just mentioned would be represented:



Tetrahydro-cupric ion; Hypochlorite ion; Chlorate ion; Perchlorate ion; Hydrogen disulfide; Hydrogen trisulfide

The central particle in the ions in this list is shown by X-ray examination of crystals to be identically bonded with all the oxygen atoms that surround it. Assume that the central particle starts as a neutral atom, which first acquires the charge to be possessed by the ion as a whole, then forms coordinate bonds with its neighbors. Covalent bonds also account for the fact that the halides of trivalent metals usually form doubled molecules, such as Al_2Cl_6.



A coordinate or semi-polar bond is really intermediate between ionic (polar) and covalent (non-polar) bonding. We may think of it as being formed by first transferring an electron from an atom (A) having an unused pair of electrons to another atom (B), then linking the two ions thus formed by an ordinary covalent bond in which each ion furnishes an electron. Thus we obtain $A^+—^-B$, which we formerly represented by $A \rightarrow B$. The first of these two methods of representing the coordinate or semi-polar bond is tending to be preferred.

Measurements of the "bond length" or center-to-center distance between atoms shows that coordinate bonds are less frequent than they were thought to be a few years ago. So nitric and sulfuric acids are perhaps correctly represented by the formulas that were assigned to them before coordinate bonds were known:

(Ex. 15, 16)

► 251. An Important Check on Electronic Formulas

As a check on electronic formulas, observe how many electrons are apparently gained by each of the combining atoms, in forming each

type of bond, owing to the fact that each electron in the bond is counted twice (once for each atom):

	Electrons Apparently Gained by A	*Electrons Apparently Gained by B*
A—B	1	1
A=B	2	2
A≡B	3	3
A→B	0	2

As an exercise in applying this check, list the number of electrons originally possessed by each atom in forming the substances whose structural formulas are given on the preceding page; also list the number of electrons gained in forming the bonds indicated, and so determine which atoms possess octets in the completed molecules.

NORMAL COVALENT RADII

Radii of atoms linked to one or more neighboring atoms by single covalent bonds. Values are given in Ångström units. Based on the work of Pauling and Huggins (1934).

H 0.28	B 0.89	C 0.77	N 0.70	O 0.66	F 0.64
		Si 1.71	P 1.10	S 1.04	Cl 0.99
		Ge 1.22	As 1.21	Se 1.17	Br 1.14
		Sn 1.40	Sb 1.41	Te 1.37	I 1.33
		Pb 1.46	Bi 1.51		

252. Coordination

All that precedes may have led the reader to believe that the number of particles joined to a central particle, in forming a molecule or ion, is determined solely by the number of pairs of oppositely spinning electrons that happen to be available for linking the atoms together. Nothing could be further from the truth. We do, of course, need a sufficient number of paired electrons to link the atoms together, but *the central atom must be large enough for all the attached atoms to* **coordinate** *with it, namely, to make contact with it at the same time.*

Figure 99 will illustrate. In forming the compound AB or the compound AB_2, the atoms concerned may be of any size, relative to one

another. But in the compound AB_3 it is plain that the central atom, A, cannot be too small, or it will be unable to come into contact with all three atoms of B simultaneously. Calculation shows that the actual diameter of A must be at least 0.15 times that of the atoms of B.

Our figure shows that in forming the compound AB_4 there are two possibilities. If the four atoms of B all lie in the same plane, then the diameter of an atom of A must be at least 0.41 times that of an atom of

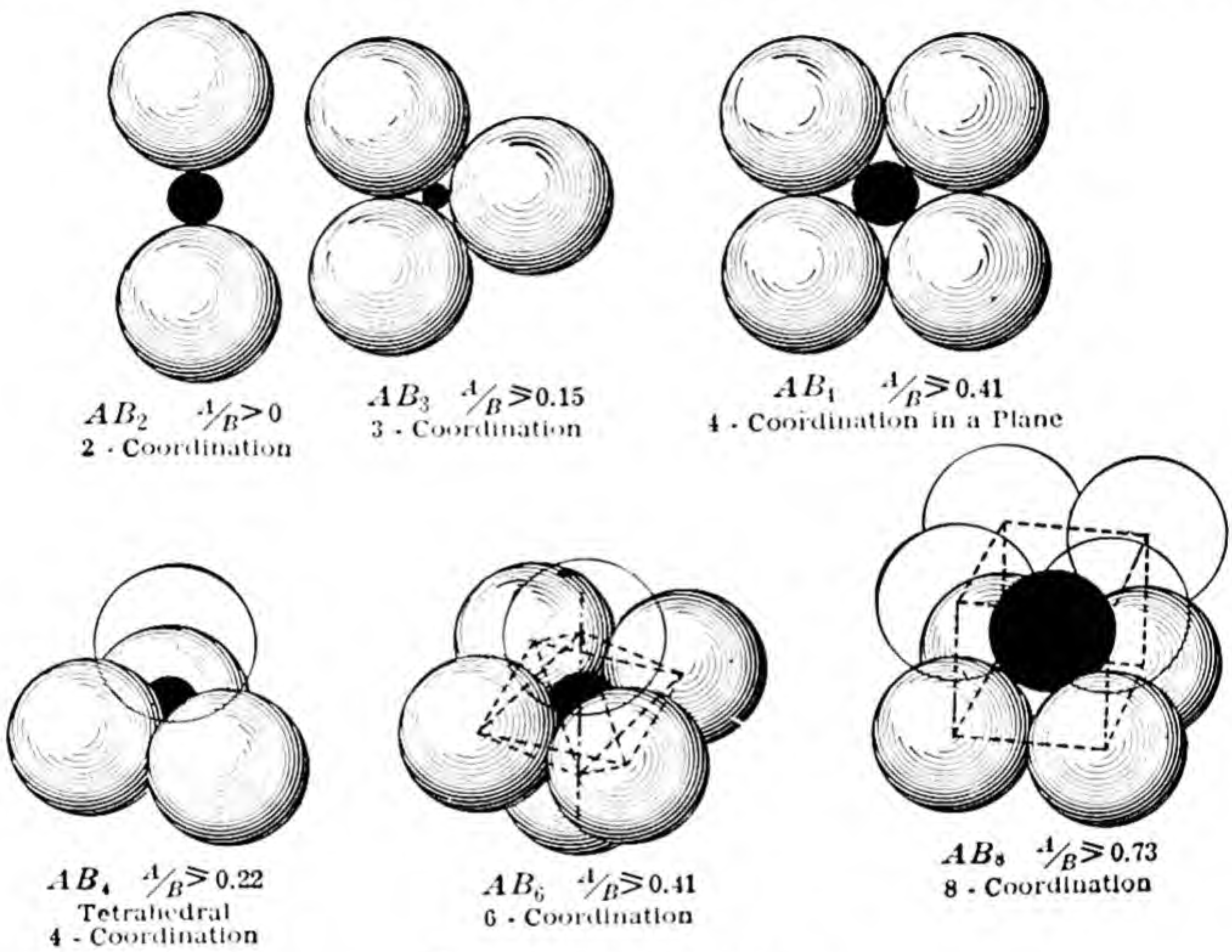


FIG. 99. Coordination.

B, if it is to make contact with all four atoms of B at once. If the four atoms of B lie at the four corners of a *tetrahedron* (triangular pyramid) the diameter of A must be at least 0.22 times the diameter of an atom of B. Most examples of 4-coordination are of the tetrahedral variety.

With the compound AB_6, a symmetrical arrangement of the atoms of B at the six corners of an *octahedron* demands that the diameter of an atom of A be at least 0.41 times the diameter of an atom of B.

The compound AB_8 is possible only if an atom of A is at least 0.73 times the diameter of an atom of B. This is cubical coordination.

In applying these rules one will always need to consider what type of bonding exists between the atoms, since the radius of any atom varies with the type of bonding. If atoms are linked by covalent bonds the table of normal covalent radii (p. 293) may be employed.

If ions are concerned, as in an ionic crystal, one may use the table of ionic radii, next following. The cations of greater charge than +2 are often called *hypothetical cations.* Their radii are calculated on the assumption that any oxygen associated with them is in the form of the oxide ion, O^{--}. They are thus unreliable for calculation of coordination, though they do give the center-to center distance between particles with fair accuracy, whenever the other particle is assumed to be the oxide ion.

IONIC RADII

We write N^{+5}, etc., rather than N^{+++++}, etc., to show that the particle, when the valence number is greater than +2, is usually incapable of existence as an independent ion, but is combined with O^{--}, F^{-}, or something else, to make a compound ion.

	Ion:	H^-	Li^+	Be^{+2}	B^{+3}	C^{+4}	N^{+5}		
	Radius:	1.27	0.6	0.31	0.20	0.15	0.11		
N^{-3}	O^{-2}	F^-	Na^+	Mg^{+2}	Al^{+3}	Si^{+4}	P^{+5}	S^{+6}	Cl^{+7}
1.44	1.40	1.36	0.95	0.65	0.50	0.41	0.34	0.29	0.26
	S^{-2}	Cl^-	K^+	Ca^{+2}	Sc^{+3}	Ti^{+4}	V^{+5}	Cr^{+6}	Mn^{+7}
	1.84	1.81	1.33	0.99	0.81	0.68	0.59	0.52	0.46
	Se^{-2}	Br^-	Rb^+	Sr^{+2}	Y^{+3}	Zr^{+4}	Cb^{+5}	Mo^{+6}	
	1.98	1.95	1.48	1.13	0.93	0.80	0.70	0.62	
	Te^{-2}	I^-	Cs^+	Ba^{+2}	La^{+3}	Hf^{+4}	Ta^{+5}	W^{+6}	
	2.21	2.16	1.69	1.35	1.15	0.79	0.71	0.65	

Linear Molecules:

O=C=O
1.28 Å 1.28 Å
Carbon Dioxide

S=C=S
1.52 1.52 Å
Carbon disulfide

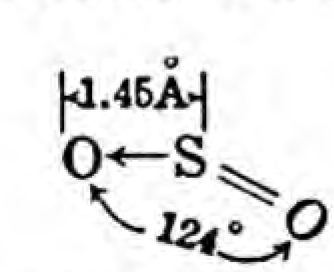
N≡N→O
Nitrous oxide

H—C≡N
1.06 1.16
Hydrogen cyanide

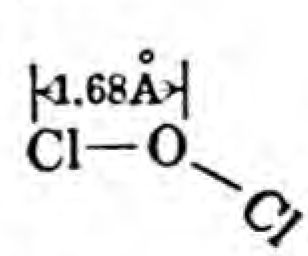
N≡C—C≡N
1.16 1.43 1.16
Cyanogen

H—C≡C—H
1.06 1.20 1.06
Acetylene

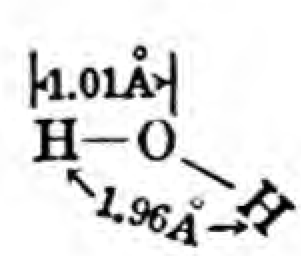
Non-Linear Planar Molecules:

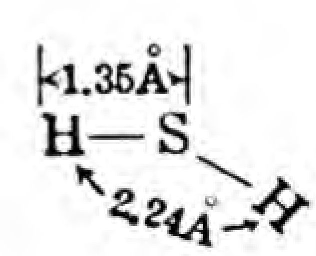


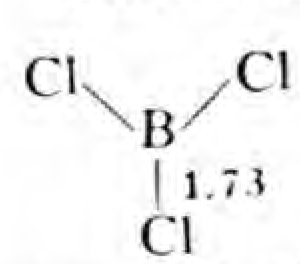
Sulfur dioxide



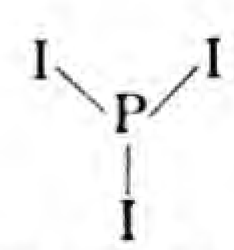
Chlorine monoxide





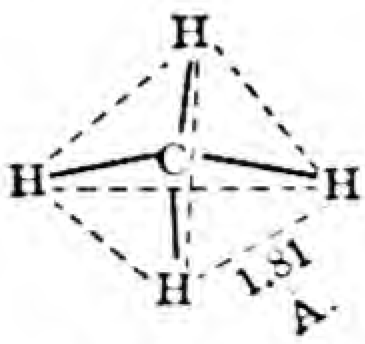


Boron trichloride

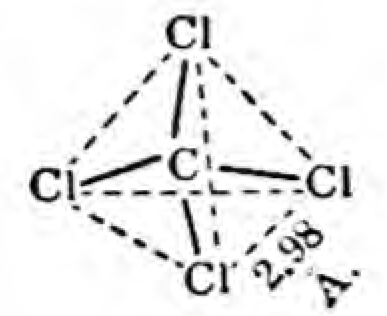


Phosphorus triiodide

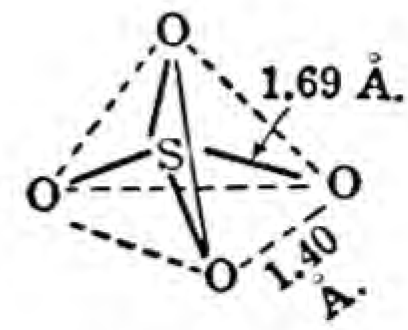
Solid Molecules of Maximum Symmetry (often termed *spherical molecules*) *Symmetrical "Top" Molecule*



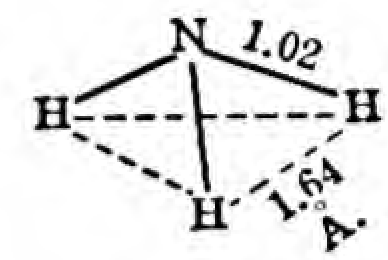
Methane



Carbon tetrachloride



Sulfate ion



Ammonia

253. Maximum Coordination Number

The *coordination number* of an atom or ion is the number of symmetrically arranged *nearest neighbors* that it has, in a crystal lattice or in a molecule, that is, the number of surrounding particles that may be considered as just touching it.

When all the atoms of a crystal are identical, as in nearly pure metals, the coordination number is frequently twelve (§ 492).

The maximum coordination number an atom may possess *in forming a compound* turns out to be:

Two for hydrogen (§ 272).

Four for the elements Li——F of the first row of eight elements of the Periodic Table.

Six for the elements, Na——Br, of the next two rows of the Periodic Table.

Eight for all elements from Rb onward.

The tendency for each element to display some favored coordination number plays almost as important a part as valence itself, in determining what molecules are capable of existence. (Ex. 17–24.)

Technical Words

Ionic valence or **electrovalence** – the valence of an ion, as indicated by its charge.

Covalence, p. 286.

Covalent linkage—a joining of two atoms by one or more pairs of oppositely spinning electrons, one member of each pair being furnished by each of the combining atoms.

Electronic formula—a formula that shows the electrons concerned in linking atoms to form molecules or ions.

Valence bond—a pair of electrons, serving to join two atoms; or the stroke or dash commonly used to represent such a pair.

Graphic formula—a formula that represents the arrangement of the atoms within a molecule in a plane or in space, together with the type of linkage that connects each atom with its neighbors.

Structural formula—a simplified graphic formula. Examples in §§ 455, 457.

Double bond, triple bond, p. 289.

Coordinate bond or **semi-polar bond**—a bond formed by a pair of electrons, both furnished by the same atom.

Complex ion—an ion produced by the direct union of simple ions, or by the direct union of a simple ion with neutral molecules (commonly excluding molecules of water).

Coordination—a symmetrical arrangement of atoms about a central atom, in the construction of a molecule or ion; or the symmetrical arrangement of ions of a given charge about an ion of opposite charge, in the construction of a crystal.

Coordination number—the number of particles that are symmetrically arranged about a central particle, making contact with it, in the construction of a molecule, ion, or crystal.

Coordinate bond number—the number of particles linked to a central particle by coordinate bonds (§ 250).

Tetrahedron (or triangular pyramid)—a solid figure having four triangular faces (and four vertices).

Octahedron—a solid figure having eight triangular faces (and six vertices).

Exercises

1. How many electrons are there in each energy level in the calcium atom and the sulfur atom? Explain what happens in the formation of calcium sulfide (an ionic compound).

2. In the formation of magnesium chloride, when chlorine gas reacts with metallic magnesium, what process supplies the energy that is required to remove the two electrons from the magnesium atom? What other source of energy would be available if magnesium were to react with chlorine in solution in water?

3. Write an electronic formula for hydrogen bromide gas, assuming covalent linkage. What inert gas has the same arrangement of electrons as the bromine atom, in a molecule of hydrogen bromide?

4. Stannic chloride, $SnCl_4$, is a volatile liquid, which is a poor conductor of electricity. What conclusion may you draw?

5. Which of the two compounds, $PbCl_2$ and $PbCl_4$, is a volatile non-conducting liquid, and which a crystalline solid, possessing fair conductivity when melted? Explain.

6. Explain why a solution of hydrogen chloride in benzene (a slightly active substance) is a non-conductor of electricity, whereas a solution of hydrogen chloride in water is a good conductor.

7. Using dots and crosses to distinguish between electrons originally furnished by hydrogen and by carbon, write an electronic formula for ethane, C_2H_6 (linking the two carbon atoms with each other, and making sure that each carbon atom acquires a complete octet).

8. Write an electronic formula for chlorine monoxide, Cl_2O, giving the oxygen atom the central position.

9. Show that there is an uncompleted octet in boron trichloride, BCl_3.

10. Write a structural formula for sulfur monochloride, S_2Cl_2, assuming that the two sulfur atoms are combined with each other and that one chlorine atom is combined with each sulfur atom.

11. Write a structural formula for ethane, C_2H_6.

12. Write an electronic formula then a structural formula for chloroform, $CHCl_3$, giving carbon a central position and combining the other atoms with it.

13. Write an electronic formula then a graphic formula for formic acid, $HCOOH$, assuming that the carbon atom is linked to hydrogen, oxygen, and hydroxyl. (Use

a double bond where necessary to insure that each atom other than hydrogen acquires a complete octet.)

14. Write a structural formula for cyanogen chloride, ClCN, in such a way as to give each atom a complete octet.

15. The extra electron in ClO_3^- or ClO_4^- may be assigned to the chlorine atom. Complete structural formulas, to give each chlorine atom an octet.

16. Write an electronic formula and the corresponding structural formula to account for hydrogen peroxide, H_2O_2, assuming that the two hydrogen atoms are linked to different oxygen atoms.

17. List electrons originally possessed and electrons apparently gained by each atom in building the formulas on p. 292.

18. Write two possible structural formulas for sulfurous acid, H_2SO_3, in one of which both hydrogen atoms are linked to oxygen, and in the other only one of them. Check these structural formulas for complete octets.

19. Rewrite the formulas given for sulfuric and nitric acids on p. 292, representing the semi-polar bond in a different manner.

20. Give an electronic formula and the corresponding structural formula to account for the thiosulfate ion, $S_2O_3^{--}$.

21. If four molecules of ammonia and two chloride ions are coordinated with a cobaltic ion, Co^{+++}, write a structural formula to indicate the charge of the complex ion so produced.

22. Write a structural formula to show how the cyanide ion, $[:C{\equiv}N:]^-$, combines with the ferrous ion to form the ferrocyanide ion $Fe(CN)_6^{----}$. Similarly, account for the ferricyanide ion, $Fe(CN)_6^{---}$.

23. Does aluminum show the maximum coordination number for its own row of the Periodic Table, in forming aluminum chloride (§ 253)?

24. Does sulfur show the maximum coordination number for its own row in the Periodic Table, in forming sulfur hexafluoride, SF_6?

Chapter 20

OXIDATION AND REDUCTION

► 254. The Reaction of Metals with Non-Metals

We have learned (§ 242) that when the most pronounced *metallic elements* (Columns 1A and 2A of the Periodic Table) react with the most pronounced *non-metallic elements* (Columns 6A and 7A) there is *a transfer of electrons from the metal to the non-metal.* Thus when magnesium burns in air or oxygen the result is magnesium oxide, an ionic compound:

$$\underset{\substack{\text{Metallic}\\ \text{magnesium}}}{2\text{Mg}} + \underset{\text{Oxygen}}{\text{O}_2} \xrightarrow{} \underbrace{2\text{Mg}^{++} + 2\text{O}^{--}}_{\substack{\text{Magnesium oxide}\\ \text{(otherwise written 2 MgO)}}} \qquad (4e \text{ from Mg to } \text{O}_2)$$

We see that each magnesium atom here transfers two electrons to an oxygen atom, thus becoming a magnesium ion, Mg^{++}, and forming an oxide ion, O^{--}.

Sodium burns vigorously in an atmosphere of chlorine, forming white fumes that are really microscopic crystals of common salt:

$$\underset{\substack{\text{Metallic}\\ \text{sodium}}}{2\text{Na}} + \underset{\substack{\text{Chlorine}\\ \text{gas}}}{\text{Cl}_2} \rightarrow \underbrace{2\text{Na}^{+} + 2\text{Cl}^{-}}_{\substack{\text{Sodium chloride}\\ \text{(otherwise written 2 NaCl)}}} \qquad (2e)$$

Here each sodium atom transfers an electron to a chlorine atom.

Iron filings, mixed with sulfur, burn vigorously when the mixture is heated, forming ferrous sulfide:

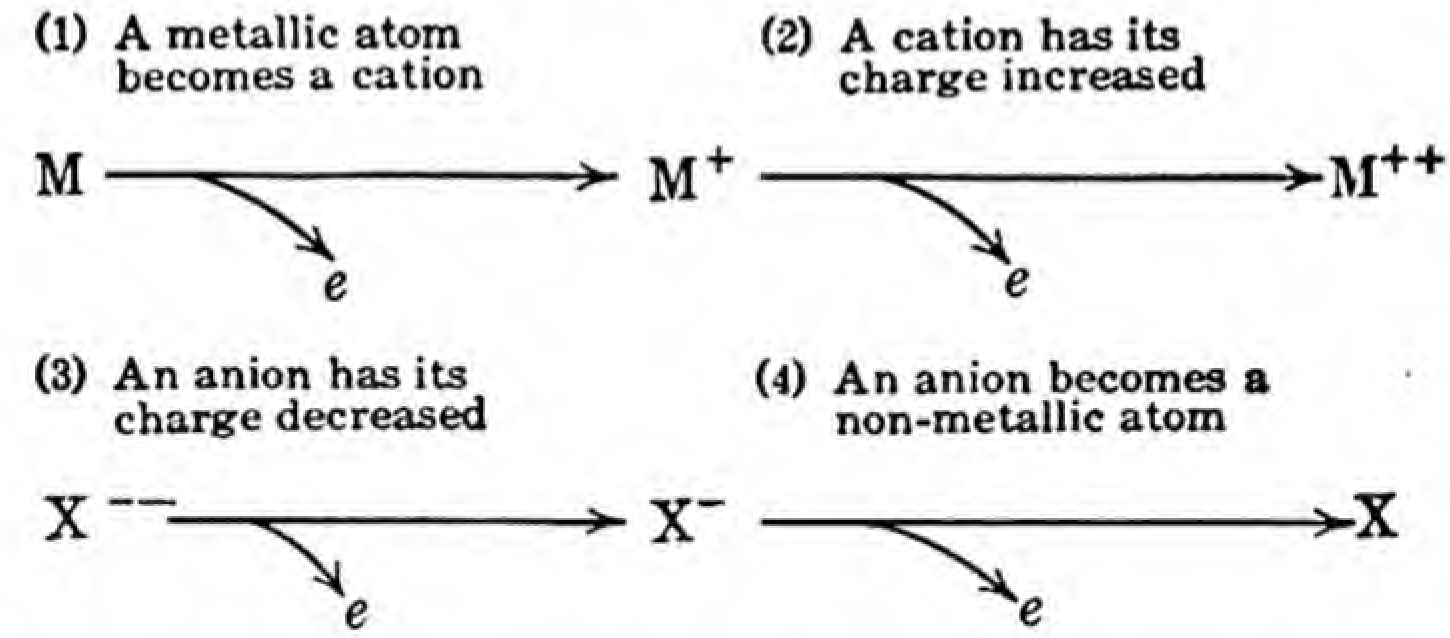
$$\text{Fe} + \text{S} \rightarrow \underbrace{\text{Fe}^{++} + \text{S}^{--}}_{\text{Ferrous sulfide}} \qquad (2e)$$

Here each iron atom transfers two electrons to a sulfur atom. (Ex. 1, 2.)

► 255. Broadened Definitions of Oxidation and Reduction

In an earlier chapter (§ 53) we noted that the word oxidation, which originally referred to direct union with oxygen, was finally broadened to include *direct union with any non-metal.* But we have just seen that the oxidized element, in such reactions, *loses electrons.* So *oxidation* has finally come to mean *any reaction in which a given substance loses electrons or a share in electrons.* Conversely, *reduction,* in the most general sense, is *any reaction in which a given substance gains electrons or a share in electrons.*

Simplest examples of oxidation (loss of electrons):



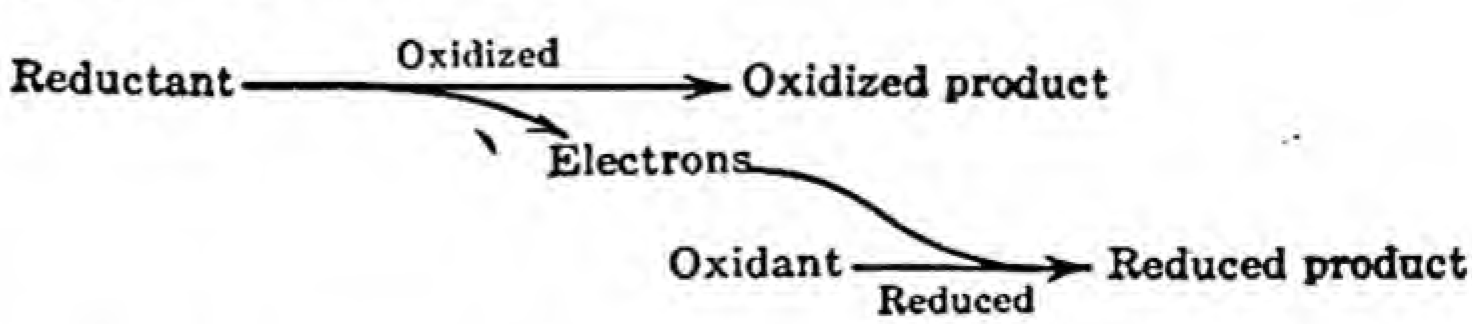
The reverse cases, left for the reader to state, are the simplest examples of reduction. (Ex. 3–5.)

Oxidation and reduction always occur together, since the electrons that one substance loses must be gained by another. Reactions in which electrons are transferred are therefore termed *oxidation-reduction reactions*, or sometimes, briefly, *redox reactions.*

A substance that yields electrons to something else (and so compels something else to gain electrons or be reduced) is called a *reducing agent* or *reductant.* In losing electrons it is itself *oxidized.*

A substance that gains electrons (and so compels something else to lose electrons or be *oxidized*) is called an *oxidizing agent* or *oxidant.* In gaining electrons it is itself *reduced.*

Electrons are always transferred from the reducing agent (reductant) to the oxidizing agent (oxidant):



► 256. Oxidation and Reduction in Terms of Valence Numbers

In defining *oxidation as a loss of electrons* and *reduction as a gain of electrons* we never encounter any difficulties so long as we are forming

or discharging ions, or sharing electrons to form semi-polar bonds (§ 250), in which one atom is definitely positive and the other definitely negative. The atom that has been made more positive has been *oxidized*, and the one that has been made more negative has been *reduced*.

But what shall we say of the formation of a covalent bond, in which *each atom* yields to the other what so far as we know is an even share in one or more electrons? Which atom has been oxidized and which reduced, when phosphorus and hydrogen (ordinarily, *both* reducing agents) combine to form PH_3; or when oxygen and chlorine (ordinarily, *both* oxidizing agents) combine to form Cl_2O?

To escape from this difficulty we may rather arbitrarily define *oxidation* as a reaction in which *valence number* (valence as given by an arbitrary rule, § 171) becomes less negative or more positive, and *reduction* as a reaction in which valence number becomes less positive or more negative. Then in forming PH_3 from the elements we may say that phosphorus is being *reduced* from a valence number of 0 to one of -3, since the valence number of hydrogen is to be arbitrarily taken as $+1$. (Ex. 6.)

Similarly we would have to regard chlorine as being *oxidized* by oxygen, in forming Cl_2O, since its valence number increases from 0 to $+1$, in spite of the fact that oxygen is a less active oxidizing agent than chlorine. We will even meet unimportant compounds, such as S_2Br_2, S_4N_4, and FNO_3, in which the valence numbers of the combining elements are undefined by the ordinary rules.

Reactions in which there is no change in valence number are not to be classed as oxidation-reduction. For example, there is no change in valence number in most instances in which ions produce a precipitate:

$$2Ag^+ + CrO_4^{--} \rightarrow Ag_2CrO_4 \downarrow$$
$$Fe^{+++} + 3OH^- \rightarrow Fe(OH)_3 \downarrow$$

▶ 257. Oxidation of Metals in Reacting with Acids

Review §§ 88, 90.

When a metal reacts with an acid, as in

$$\underset{\text{Metallic zinc}}{Zn} + \underset{\text{Any acid}}{2H^+} \rightarrow \underset{\text{A zinc salt}}{Zn^{++}} + \underset{\text{Hydrogen gas}}{H_2 \uparrow}$$

the metal always loses electrons (or at least a share in electrons, as in forming a covalent salt, such as Al_2Cl_6). In brief, *a metal, in reacting*

with an acid, is always oxidized. Ordinarily the electrons yielded by the metal are transferred to the protons of the acid, as shown in the preceding equation, thus yielding *hydrogen gas.*

Concentrated sulfuric acid, nitric acid of any concentration, and a few other acids are sometimes termed *oxidizing acids.* But we have just seen that *all* acids really oxidize metals that react with them. The significant thing about nitric acid or concentrated sulfuric acid is that metals reacting with them transfer electrons, not to protons, but to *anions of the acid or to acid molecules.* In consequence, these acids will react *even with the first few metals below hydrogen in the electrochemical series.* They do not yield hydrogen when they react with such metals. Instead we obtain *sulfur dioxide gas* or *one of the oxides of nitrogen:*

$$\underbrace{2H_2SO_4}_{\text{Hot, concentrated sulfuric acid *}} + \underset{\text{From metal}}{2e} \rightarrow SO_2\uparrow + 2H_2O + \underset{\text{A metallic sulfate}}{SO_4^{--}}$$

$$\underbrace{4NO_3^- + 4H^+}_{\text{Dilute nitric acid}} + \underset{\text{From metal}}{3e} \rightarrow \underset{\text{Nitric oxide}}{NO\uparrow} + 2H_2O + \underset{\text{A metallic nitrate}}{3NO_3^-}$$

* Dilute sulfuric acid, reacting with metals, yields hydrogen rather than sulfur dioxide.

► 258. Displacement of One Metal by Another

If a sheet of zinc or iron is placed in a solution of copper sulfate it soon becomes covered with metallic copper. We may think of the zinc or iron as having passed into solution and as having *displaced* the copper from the copper salt:

$$Fe + CuSO_4 \rightarrow FeSO_4 + Cu\downarrow$$

Reactions of this sort are useful in recovering a more expensive metal from a solution of one of its salts, at the cost of a less expensive metal. Thus copper has sometimes been recovered from dilute solutions of copper salts by the use of scrap iron; and silver is sometimes recovered from waste photographic solutions by treating them with metallic zinc or copper. Other examples are shown in Fig. 100.

Such **metallic displacements** are really accomplished by *a transfer of electrons from atoms of one metal to the ions of another:*

$$\underset{\text{Metallic iron}}{Fe} + \underset{\text{A cupric salt}}{Cu^{++}} \xrightarrow{} \underset{\text{A ferrous salt}}{Fe^{++}} + \underset{\text{Metallic copper}}{Cu^{\circ}}$$

The *activity series*, which we formerly used (§ 88) to predict which metals react most readily with acids or with water, will also tell us which metals displace others from solutions of their salts. Roughly stated, *any metal will displace any other metal, occupying a lower position in the activity series, from a solution of any of the salts of the second metal, provided that the metal to be displaced is not very far above hydrogen* (when an aqueous solution is employed).

Thus metals above copper in the activity series will transfer electrons to cupric ions and hence will displace metallic copper from a solution of a cupric salt. Similarly, metallic copper will displace gold or silver from a solution of any gold or silver salt. But zinc or iron is not effectively displaced from an aqueous solution of a zinc salt or ferrous salt (using sodium or magnesium, for example, as the displacing element). Instead, hydrogen gas is displaced from the water itself, since hydrogen is much lower in the series than either zinc or iron. (Ex. 7–11.)

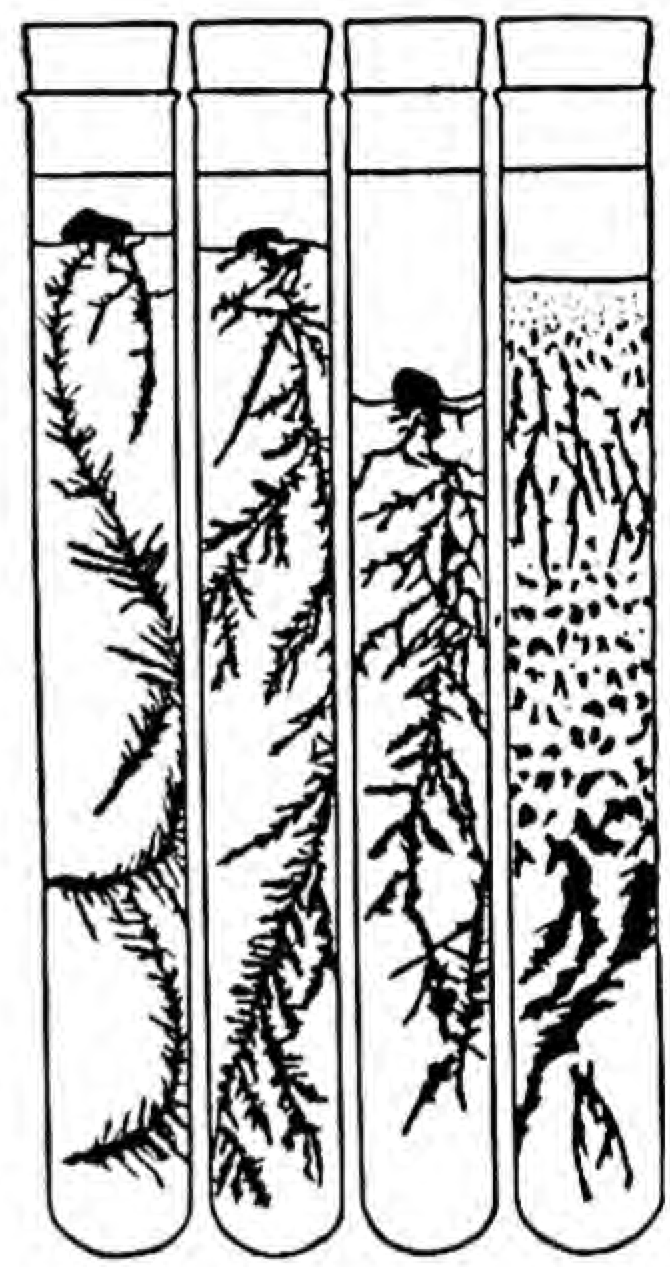


FIG. 100. Crystals of metallic lead (left) and metallic silver (right), produced by placing fragments of metallic zinc on top of silica gel (§ 483) that contains a silver salt or a lead salt. The zinc dissolves, forming a zinc salt (Zn^{++}) and the silver or lead separates in metallic form.

259. What Determines the Position of a Metal in the Activity or Electrochemical Series

We can now readily see that the activity series is not merely a list of the metals in the order of decreasing tendency to be oxidized (that is, in the order of decreasing tendency to lose electrons). It is a list of the metals in the order of *decreasing tendency to lose electrons and pass into solution as hydrated ions.* Three different steps are really involved, though they take place simultaneously:

1. Solid metal must be dispersed as separate atoms (as in a vapor).
2. The atoms must lose electrons, thus forming cations.
3. The cations then become hydrated, and dissolve.

The first two processes demand energy; the third yields energy.

The *alkali metals* and *alkaline-earth metals* are soft and weak, hence ittle energy needs to be expended in the first stage (tearing down the rystal lattice). Furthermore, the third stage (except for lithium) is

never very pronounced for these metals. In consequence, the second stage (loss of electrons, § 238) is the one that chiefly determines the position of the alkali metals and alkaline-earth metals in the electrochemical series. Those of largest atomic radius yield electrons most readily, and so stand highest in the series.

But the lithium ion, Li^+, because of its small radius, can bind water so firmly, in other words releases so much energy in being hydrated, that the net demand for energy is much reduced; for this reason lithium is the most active of the alkali metals, whereas it would otherwise be the least active.

The *heavy metals* form strong and hard crystals; hence the first stage (tearing down the crystal lattice) usually demands almost as much energy as the third stage (hydration of the cations) can furnish. This is the chief reason why silver occupies a position well below hydrogen in the electrochemical series, in spite of the fact that the silver atom very readily loses an electron.

► 260. Electrochemical Oxidation and Reduction

Whenever an electric current is passed through a *solution* (or a *molten salt* or *alkali*) chemical changes take place at both electrodes. The electrode into which electrons enter the solution from the outer circuit is the *cathode* (*C*, Fig. 101). Something in contact with the cathode (or occasionally the material of the cathode itself) is made to accept these electrons or be *reduced*. The electrode from which the electrons leave the solution and return to the outer circuit is the *anode*. The material of the anode itself or something in contact with it is made to lose these electrons or to be *oxidized*.

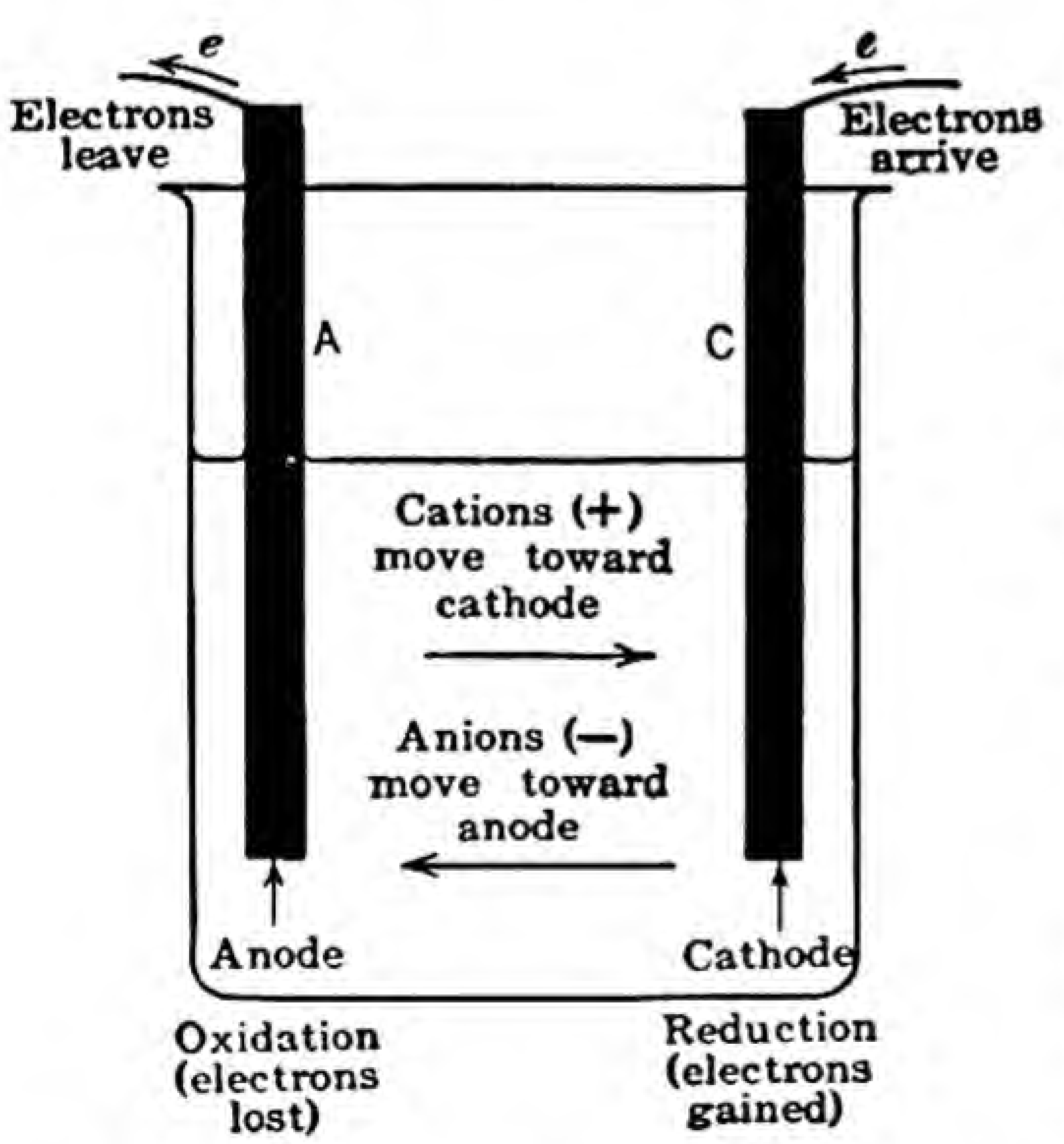


FIG. 101. Electrochemical oxidation and reduction.

It is best to speak of an electrode as *cathode* or *anode* according as electrons there enter or leave the solution. Avoid the terms *positive* and *negative electrode*, because of risk of confusion. (More about this in § 515.)

Reduction always takes place at the cathode and oxidation at the anode. Study Fig. 101 until it is familiar in all its details. (Ex. 12–14.)

However far apart the electrodes may be, reduction at the cathode and oxidation at the anode always involve the same number of electrons. Figure 102 shows an imagined experiment in which a flow of current is supposed to be set up in a Pacific cable by attaching the San Francisco end of the cable to a rod of metallic zinc dipping into dilute sulfuric acid, and the Australian end to a rod of copper dipping into a copper sulfate solution. The return circuit is made through the ocean itself, as shown. When the circuit is closed, electrons yielded by the zinc in San Francisco enter the cable while the same number of other electrons in Australia is being accepted by cupric ions:

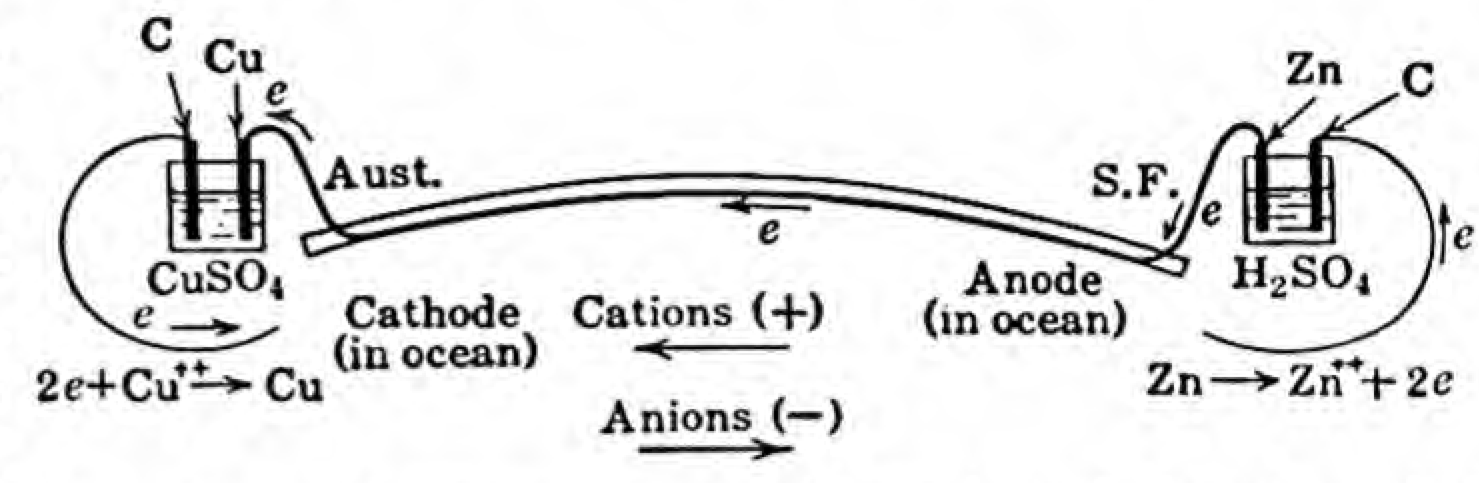


FIG. 102. Oxidation, in San Francisco, is here coupled with reduction, in Australia.

$$\underset{\text{Metallic zinc}}{Zn} \rightarrow \underset{\text{Zinc ions}}{Zn^{++}} + 2e \quad \text{(Oxidation)}$$

$$\underset{\text{Cupric ions}}{Cu^{++}} + 2e \rightarrow \underset{\text{Metallic copper}}{Cu} \quad \text{(Reduction)}$$

Meanwhile, all the ions in the Pacific Ocean acquire a small extra component of motion (toward San Francisco for the anions and toward Australia for the cations). It would take any of these ions thousands of years to cross the ocean, though the electric field that sets them in motion is established with the speed of light.

The final result is that metallic zinc passing into solution in San Francisco (oxidation) displaces copper from solution in Australia (reduction). Moreover, 1 gram atom (65 grams or 6×10^{23} atoms) of zinc dissolves for each gram atom (63.5 grams or 6×10^{23} atoms) of copper separated. But the ions concerned (Zn^{++} and Cu^{++}) are both doubly charged. So *twice* 6×10^{23} electrons will have passed into the San Francisco end of the cable and the same number out at the Australian end. (Ex. 15.)

► 261. Important Reductants (Electron Donors)

Here is a preliminary view of a few common reductants. The important thing to be remembered for each is the *name and formula of the oxidized product* that is formed when the reductant parts with one or more electrons. Here and in what follows we shall use the

symbols K^+, Fe^{++}, Zn^{++}, etc., to represent cations that are presumed actually to exist; and the symbols Al^{+3}, Sn^{+4}, Mn^{+7}, etc., to represent *hypothetical cations*, in which the element has the indicated valence number, but is actually combined with other atoms, as in Al_2Cl_6 and MnO_4^-.

Reductants	*Oxidized Products*	*Reductants*	*Oxidized Products*
Sn^{++}	Sn^{+4}	AsO_2^- Arsenite ion	AsO_4^{---} Arsenate ion
SnO_2^{--} Stannite ion	SnO_3^{--} Stannate ion	$C_2O_4^{--}$ Oxalate ion	$2CO_2$ Carbon dioxide gas
Fe^{++}	Fe^{+3}	H_2O_2 Hydrogen peroxide	$O_2 + 2H^+$
$2I^-$	I_2	Zn, Al (and other active metals)	Zn^{++}, Al^{+3}
H_2S	S (and H_2O or H^+)	CO (at high temperatures)	CO_2
H_2S	SO_4^{--} (when the most active oxidizing agents are used)		
SO_2 or SO_3^{--}	SO_4^{--}	H_2 (at high temperatures)	H_2O
NO_2^- Nitrite ion	NO_3^- Nitrate ion		

► 262. Electronic Equations

When a stannous salt is converted into a stannic salt, the ion Sn^{++} must lose 2 electrons:

$$Sn^{++} \rightarrow Sn^{+4} + 2e$$

Similarly, an atom of metallic aluminum must lose three electrons in being converted into Al^{+3}:

$$Al \rightarrow Al^{+3} + 3e$$

Check by noting that each side of the equation is now electrically neutral, since the electrons count as negative charges. (Ex. 16.)

Such *electronic equations* are sometimes referred to as *half equations*, since the electrons represented as being set free by the reductant must actually be accepted by something else (serving as oxidant), in a separate reaction. We shall presently see how two half equations, one representing the loss of electrons by the reductant, the other the gain of electrons by the oxidant, may be combined to form an ionic equation for the complete reaction (§ 265).

Let us next consider an example in which the reductant not only loses electrons but also gains oxygen, as when SO_2, in serving as a reducing agent, is itself oxidized to SO_4^{--}. *We may usually consider oxygen gained as having been furnished by water.* For SO_2 to be converted into SO_4^{--}, 2 molecules of water are needed, the hydrogen of the water being rejected as ***protons*** on the opposite side of the equation. Thus we have

$$SO_2 + 2H_2O \rightarrow SO_4^{--} + 4H^+ \quad \text{(incomplete)}$$

The final step is to add enough electrons to one side to balance the equation electrically. The left-hand side of the reaction just written is electrically neutral; the right-hand side has a surplus of 2 positive charges. We therefore add 2 electrons (that is, 2 negative charges) on the right, and thus obtain for our balanced half equation:

$$SO_2 + 2H_2O \rightarrow SO_4^{--} + 4H^+ + 2e$$

Observe that the sulfur dioxide *loses* 2 electrons in serving as a *reductant*, though incidentally combining with $2O^{--}$, derived from water. (Ex. 17, 18.)

► 263. Important Oxidants (Electron Acceptors)

Here is a preliminary view of a few important oxidants, to be studied with the same care that has just been indicated for reductants:

Oxidants	*Reduced Products*	*Oxidants*		*Reduced Products*
Cl_2, Br_2, I_2 Halogens	Cl^-, Br^-, I^- Halide ions	H_2O_2 Hydrogen peroxide		H_2O
NO_2^- Nitrite ion	NO Nitric oxide			
NO_3^- (or HNO_3) Nitrate ion, in acid solution	NO_2 or NO (but see § 380)	ClO^- Hypochlorite ion		Cl^-
H_2SO_4 (conc.)	SO_2	BrO^- Hypobromite ion		Br^-
MnO_4^-	Mn^{++} (acid solution)			
MnO_4^-	MnO_2 (alkaline solution)	NO_3^- Nitrate ion	In alkaline fusions at high temperatures	NO_2^- Nitrite ion
$Cr_2O_7^{--}$	Cr^{+3}	ClO_3^- Chlorate ion		Cl^-
CrO_4^{--}	Cr^{+3}	O_2^{--} Peroxide ion		O^{--}

Observe that hydrogen peroxide (valence number of oxygen, -1) serves as a reductant in some reactions (§ 261) and as an oxidant in others. The same is true of nitrite ion (valence number of nitrogen, $+3$) and of many other substances in which some element happens to possess a valence number *intermediate* between the highest and the lowest that are possible for that element—since in serving as a reductant an element is oxidized and its valence number is increased, whereas in serving as an oxidant the element is reduced and its valence number is decreased (§ 256). (Ex. 19.)

► 264. More Electronic Equations

When an oxidizing agent gains electrons it may concurrently lose oxygen, as in converting NO_2^- into NO. It is usually best to consider this oxygen as being lost by combining with *protons* (always present in an acid solution, and in traces even in an alkaline solution), the product being *water:*

$$NO_2^- + 2H^+ \rightarrow NO + H_2O \quad \text{(incomplete)}$$

The final step is to balance the equation electrically, by adding electrons. The right-hand side is electrically neutral; the left-hand side has a surplus of one positive charge. We offset this by adding 1 electron (a negative charge) to the left-hand side, thus obtaining the balanced half equation:

$$NO_2^- + 2H^+ + e \rightarrow NO + H_2O$$

When a dichromate, $Cr_2O_7^{--}$, is reduced to a chromic salt, Cr^{+3}, we need to remove 7 atoms of oxygen, by combining them with 14 protons:

$$Cr_2O_7^{--} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O \quad \text{(incomplete)}$$

(observing that $Cr_2O_7^{--}$ must give $2Cr^{+3}$). Our final step is to balance the equation electrically. On the left we have a surplus of 12 positive charges; on the right only 6. We must therefore add 6 electrons (negative charges) on the left. Thus we obtain the balanced half equation:

$$Cr_2O_7^{--} + 14H^+ + 6e \rightarrow 2Cr^{+3} + 7H_2O$$

(Ex. 20–23.)

► 265. Balancing Equations Involving Oxidation and Reduction

Equations involving oxidation and reduction are readily balanced with the aid of balanced half equations, one showing the loss of electrons by the reductant, the other the gain of electrons by the oxidant. For example, when sulfur dioxide reduces a chlorate to a chloride, the two balanced half equations are:

$$SO_2 + 2H_2O \rightarrow SO_4^{--} + 4H^+ + 2e$$

$$ClO_3^- + 6H^+ + 6e \rightarrow Cl^- + 3H_2O$$

The first equation yields only 2 electrons while the second demands 6; we therefore multiply the first one by 3, thus:

$$3[SO_2 + 2H_2O \rightarrow SO_4^{--} + 4H^+ + 2e]$$

The whole equation is multiplied by the 3 outside the brackets. Then, on adding this half equation, representing electrons lost by the reductant, to the preceding one, representing electrons gained by the oxidant, the electrons cancel out completely, and H^+ and H_2O partially cancel out. Thus we obtain:

$$3SO_2 + ClO_3^- + 3H_2O \rightarrow 3SO_4^{--} + Cl^- + 6H^+$$

The student should perform this addition to make sure that the result is as given. *As a final check, count atoms and charges:* 12 atoms of oxygen and 6 of hydrogen on each side of the equation; a net charge of 1 negative on each side of the equation.

Next consider a reaction in which hydrogen sulfide in a dilute acid solution reduces a permanganate. The table in § 261 indicates that hydrogen sulfide, under these conditions, is oxidized to free sulfur, S° (and H^+). Adding 2 electrons on the right, to make the half equation balance electrically, we have:

$$H_2S \rightarrow S^\circ + 2H^+ + 2e$$

Turning to § 263 we find that a permanganate in an acid solution is reduced to a manganous salt, Mn^{++}. Balancing this as already described we obtain:

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{++} + 4H_2O$$

Check this by counting atoms then electrical charges (a net charge of 2 positive on each side of the equation).

We now observe that the reductant yields only 2 electrons whereas the oxidant demands 5. So let us multiply the first half equation by 5 and the second by 2. Thus we obtain:

$$5[H_2S \rightarrow S^\circ + 2H^+ + 2e]$$

$$2[MnO_4^- + 8H^+ + 5e \rightarrow Mn^{++} + 4H_2O]$$

The 5 and the 2 multiply everything in their respective half equations. If we now add, the 10 electrons furnished by the reductant just supply the 10 needed by the oxidant. Hence electrons completely cancel out, protons partially cancel out, and we have:

$$5H_2S + 2MnO_4^- + 6H^+ \rightarrow 5S^\circ + 2Mn^{++} + 8H_2O$$

As a check, count atoms: 5 of sulfur, 8 of oxygen, 16 of hydrogen on each side of the equation; and a net charge of 4 positive on each side.

If the generalized or ionic equation just given is to be rewritten in specialized form, we need only replace $2MnO_4^-$, which refers to *any permanganate*, by the formula of some chosen permanganate, such as $2KMnO_4$ for potassium permanganate, and replace $6H^+$, which refers to *any acid*, by the formula of some chosen acid, such as $3H_2SO_4$ for sulfuric acid. If we use sulfuric acid, the manganese salt represented by $2Mn^{++}$ will obviously be manganese sulfate, $2MnSO_4$. The two potassium atoms just introduced on the left will then need to appear as K_2SO_4 on the right. The balanced equation is then:

$$5H_2S + 2KMnO_4 + 3H_2SO_4 \rightarrow 5S^\circ + 2MnSO_4 + K_2SO_4 + 8H_2O$$

Here, as usual, the specialized equation shows a substance (K_2SO_4) that did not appear in the ionic equation. (Ex. 24–26.)

266. Valence State Equations

The method just described for balancing equations involving oxidation and reduction is the one best suited to emphasize the *loss of electrons by the reductant* and the *gain of electrons by the oxidant.* The student is going to get considerable practice in the application of this method as he encounters various reductants and oxidants in succeeding chapters. In the end he should become familiar with a somewhat simpler method. In § 195 we summarized the chief reactions of chlorine in a table showing the various valence numbers or valence states of that element. Chlorine has a valence number of +1 in Cl_2O, $HClO$, ClO^-. Thus any one of these three substances may be represented by the generalized symbol Cl^{+1}.

Similarly arsenic in As_2O_3, H_3AsO_3, and AsO_2^- possesses the valence number $+3$. Any one of these substances may be represented by the generalized symbol As^{+3}. Now let As^{+3}, serving as a reductant, react with a hypochlorite, *i.e.*, Cl^{+1}, serving as an oxidant. The table in § 261 shows that the former will be oxidized to an arsenate, *i.e.*, As^{+5}, whereas the latter (§ 263) will be reduced to a chloride, Cl^-. Thus we have

Loss, 2

$$As^{+3} + Cl^{+1} \rightarrow As^{+5} + Cl^{-}$$

Gain, 2

The arsenic gains 2 units of valence number, the chlorine loses 2 units; hence the equation balances as it stands. As a check count charges: a net charge of 4 positive on each side.

As another example, let us use hydrogen sulfide or any other sulfide, in other words S^{-2}, as a reductant, to reduce a strong solution of nitric acid or a nitrate, in other words, N^{+5}. The reductant will be oxidized to a sulfate or sulfuric acid, namely S^{+6}, and the oxidant will be reduced to nitrogen dioxide, NO_2, in other words N^{+4}. We then have:

Loss, 1

$$S^{-2} + N^{+5} \rightarrow S^{+6} + N^{+4} \quad \text{(unbalanced)}$$

Gain, 8

Observe how the sulfur atom, in being *oxidized*, *gains* 8 units in valence number (actually a *loss* of 8 electrons), whereas the nitrogen, in being *reduced*, *loses* 1 unit in valence number (actually a *gain* of 1 electron). To make the loss equal to the gain we need 1 atom of sulfur for every 8 atoms of nitrogen:

$$S^{-2} + 8N^{+5} \rightarrow S^{+6} + 8N^{+4}$$

As a check, observe that the equation now balances with respect to electrical charges (38 positive charges, net, on each side of the equation).

Such *valence state equations* concentrate on the most important thing that occurs in oxidation-reduction, namely, the *transfer of electrons* or the consequent *changes in valence number*. *It is important for the student to pause to acquire a little skill in writing such equations before going further.* (Ex. 27.)

267. Relative Activities of Different Reductants and Oxidants

The tendency of a substance to be oxidized, forming a specified product, is measured by what is called its *oxidation potential* (p. 315), in volts. In the table on the opposite page the readily oxidized substances, that is, the most active reductants, are those toward the top of the left-hand column. Descending this column we encounter less and less active reductants, corresponding to decreasing positive values of the oxidation potential. The least active reductants, toward the bottom of the left-hand column, are those classed as *reduced products* in previous discussions.

The most active oxidants are those toward the bottom of the right-hand column, corresponding to high negative values of the oxidation potential. The least active oxidants are the *oxidized products* of our previous discussions.

Our table includes the metals (left-hand column) in the order of decreasing tendency to pass into solution as hydrated cations, liberating hydrogen gas. It is therefore an extension of the electrochemical series (§ 88).

This table will be found very useful in predicting reactions: *When a reductant occupies a higher position in the left-hand column than an oxidant does in the right-hand column, the former may be expected to reduce the latter.* (Nevertheless, the reaction sometimes fails to take place except in the presence of a catalyst.) For example, metallic zinc, Zn, in the left-hand column, occupies a higher position than ferric ion, Fe^{+3}, in the right-hand column. Zinc may therefore be expected to reduce ferric ion to ferrous ion, the reaction products being Zn^{++} and Fe^{++}, as indicated in the table:

$$Zn + 2Fe^{+3} \rightarrow Zn^{++} + 2Fe^{++}$$

Similarly, stannous ion, Sn^{++}, occupies a higher position in the list of reductants than free iodine in the list of oxidants. The former may therefore be expected to reduce the latter, the reaction products being as indicated in the table:

$$Sn^{++} \rightarrow Sn^{+4} + 2e$$

$$I_2 + 2e \rightarrow 2I^-$$

Adding: $$Sn^{++} + I_2 \rightarrow Sn^{+4} + 2I^-$$

On the contrary, manganous ion, Mn^{++}, occupies a lower position in the list of reductants than free iodine in the list of oxidants; hence

the reactions expressed by the two half equations

$$Mn^{++} \rightarrow Mn^{+7} + 5e$$

$$I_2 + 2e \rightarrow 2I^-$$

will not take place. The reverse reactions, on the contrary, take place readily. In other words, iodides readily reduce permanganates to manganous salts, and are themselves oxidized to free iodine. (Ex. 28.)

TABLE OF STANDARD OXIDATION AND REDUCTION POTENTIALS

Oxidation Potential (Volts) at 25°C	*Oxidizable Substances (A)*	Oxidation (Anodic) ⇌ Reduction (Cathodic)	*Reducible Substances (B)*	*Reduction Potential (Volts) at 25°C*
3.02	Li	⇌	$Li^+ + e$	−3.02
2.922	K	⇌	$K^+ + e$	−2.922
2.712	Na	⇌	$Na^+ + e$	−2.712
2.34	Mg	⇌	$Mg^{++} + 2e$	−2.34
1.67	Al	⇌	$Al^{+3} + 3e$	−1.67
0.762	Zn	⇌	$Zn^{++} + 2e$	−0.762
0.440	Fe	⇌	$Fe^{++} + 2e$	−0.440
0.402	Cd	⇌	$Cd^{++} + 2e$	−0.402
0.250	Ni	⇌	$Ni^{++} + 2e$	−0.250
0.136	Sn	⇌	$Sn^{++} + 2e$	−0.136
0.126	Pb	⇌	$Pb^{++} + 2e$	−0.126
0.000	H_2	⇌	$2H^+ + 2e$	0.000
−0.15	Sn^{++}	⇌	$Sn^{+4} + 2e$	0.15
−0.345	Cu	⇌	$Cu^{++} + 2e$	0.345
−0.401	$4OH^-$	⇌	$O_2 + 2H_2O + 4e$	0.401
−0.55	$2I^-$	⇌	$I_2 + 2e$	0.55
−0.771	Fe^{++}	⇌	$Fe^{+3} + e$	0.771
−0.7995	Ag	⇌	$Ag^+ + e$	0.7995
−0.96	$NO + 2H_2O$	⇌	$NO_3^- + 4H^+ + 3e$	0.96
−1.05	$2Br^-$	⇌	$Br_2 + 2e$	1.05
−1.36	$2Cr^{+3} + 7H_2O$	⇌	$Cr_2O_7^{--} + 14H^+ + 6e$	1.36
−1.358	$2Cl^-$	⇌	$Cl_2 + 2e$	1.358
−1.52	$Mn^{++} + 4H_2O$	⇌	$MnO_4^- + 8H^+ + 5e$	1.52
−2.85	$2F^-$	⇌	$F_2 + 2e$	2.85

Order of increasing vigor as reductants
Order of increasing ease of oxidation
Reductants
Reduced Products
Hydrogen (Acid range)
(Alkaline range)
Oxidized Products
Oxidants
Order of increasing vigor as oxidants
Order of increasing ease of reduction

The oxidation potential of an ion is a measure of its tendency to be oxidized when it is present in a solution of unit effective concentration (activity, § 419). The other electrode is assumed to be a hydrogen electrode in which hydrogen gas, under 1 atmosphere of effective pressure, is in equilibrium with hydrogen ion, in unit effective concentration.

268. Oxidation-Reduction Indicators

It is often important to know when we have added just sufficient oxidant to oxidize a given quantity of reductant. Sometimes this is easy. If an acid solution of a permanganate is slowly added from a buret to a measured quantity of a sulfite the products of the reaction happen to be colorless, hence the color of the permanganate fades away as fast as permanganate is added. But when just enough has been added to oxidize the sulfite the reaction comes to an end. The next drop of permanganate solution then persists, and colors the solution a distinct pink. This is the *end point* of the reaction.

Similarly, in oxidizing many substances with a solution of iodine, the yellow or brown color of the iodine fades away as fast as iodine is added, until the end point is reached. The next drop then turns the solution a pale yellow color; or in the presence of a little starch solution, a trace of iodine in excess will color the solution blue. This is the end point.

In the two reactions just described a colored oxidizing agent, in the presence of colorless reaction products, serves as its own *indicator*, to show when enough of the oxidizing agent has been added to complete the reaction. In other instances the oxidizing agent may be colorless, or its color at the end point may be obscured by the presence of colored reaction products (the green of chromic ion, Cr^{+3}, for example). We may then sometimes add an *oxidation-reduction indicator*—a substance which changes color sharply in the presence of a slight excess of an oxidizing agent. An example is *diphenylamine*, which in solution in sulfuric acid is greenish, but turns violet-blue in the presence of a slight excess of a strong oxidizing agent.

Another important oxidation-reduction indicator is orthophenanthroline, which with ferrous ion forms a soluble, deep red complex ion $(C_{12}H_8N_2)_3Fe^{++}$. A few drops of this indicator are added to a solution of a *reducing agent*, then an *oxidizing agent* is gradually added. As the reaction proceeds the oxidation potential (which measures the tendency of the reducing agent toward being further oxidized) continuously decreases, slowly at first, then more and more rapidly. Finally, it falls below -1.14 volts, the oxidation potential of the indicator. The next drop of the oxidizing agent then oxidizes the indicator to the deep blue complex ferric ion $(C_{12}H_8N_2)_3Fe^{+++}$. The change from pink to blue marks the end point of the titration.

Technical Words

Oxidation, p. 300. **Reduction,** p. 300.

Oxidation-reduction reaction or **redox reaction**—a reaction in which one substance (the reductant) yields electrons or a share in electrons to another substance (the oxidant).

Oxidizing acid—a colloquial term for an acid that is able to dissolve one or more metals below hydrogen in the electrochemical series. Examples: concentrated sulfuric acid, and nitric acid of any concentration. Explanation, p. 302.

Metallic displacement reaction—p. 302. Explanation, pp. 302, 303.

Cathode, p. 304. **Anode,** p. 304.

Electronic equation or **half equation**—an equation in which *electrons* appear as reactants or resultants. By combining two such equations in such proportions that electrons cancel out, we may obtain a balanced ionic equation (§ 265).

Valence state equation—an equation that indicates the changes in valence number that occur in oxidation and reduction. Examples, § 266.

Oxidation potential—a measure of the tendency of any given substance to be oxidized to some specified other substance, under specified conditions—in other words, its tendency to serve as a *reductant.*

Indicator, p. 457. **Oxidation-reduction indicator,** p. 314.

End point—the practical completion of a reaction, as made evident by the first perceptible alteration of the color of an added indicator, or in some other manner.

Exercises

1. Write an equation showing the ions produced and the transfer of electrons that occurs when magnesium burns in chlorine, forming magnesium chloride, $MgCl_2$.
2. When mercury is heated in a current of iodine vapor the two elements combine to form mercuric iodide. Write an equation to show what ions are produced and the transfer of electrons that occurs.
3. List four simple examples of reduction, the reverse of oxidation (§ 255).
4. What is an oxidized product? A reduced product?
5. Which of the following are classified as oxidation and which as reduction:

   A ferric salt is converted into a ferrous salt.
   A sulfide yields elementary sulfur.
   A stannous salt becomes a stannic salt.
   A persulfate, $S_2O_8^{--}$, becomes a sulfate, $2SO_4^{--}$.

6. What change in valence number occurs when nitric acid is converted into nitric oxide, NO? Is this oxidation or reduction?
7. Write an equation for the displacement of silver from a silver nitrate solution by means of metallic copper. Then express this as an ionic equation, in such a manner as to show the transfer of electrons.
8. Powdered metallic iron is added to a solution containing a dissolved cupric salt and a dissolved cadmium salt. Which metal will be displaced most readily and most completely? Write an ionic equation.

9. In which of the following will a metal be displaced, in which will hydrogen be displaced, and in which will no appreciable reaction occur:

Metallic copper is added to a solution of lead acetate.
Metallic zinc is added to a solution of a mercurous salt.
Metallic potassium is added to a solution of an aluminum salt.
A photographic print, consisting of a deposit of metallic silver, is dipped into a solution of gold chloride.

10. When bromine reacts with hydrogen sulfide, forming hydrogen bromide and free sulfur, which element gains and which loses a share in electrons? Which element has been oxidized and which reduced?

11. Write an equation for a reaction in which chlorine displaces iodine from a solution of magnesium iodide. Then express this as an ionic equation, showing the transfer of electrons.

12. In discharging a storage cell, at one electrode metallic lead is converted into lead ion (in lead sulfate); at the other, lead dioxide, PbO_2, is converted into lead ion. From changes in valence number, determine (§ 260) which electrode is cathode and which anode, during discharge.

The reactions at the electrodes are reversed in charging a cell. Which electrode is then cathode and which anode?

13. Sheet zinc, serving as the container, is gradually corroded in a dry cell, with the formation of a zinc salt. Is the zinc serving as anode or cathode?

14. In the Edison storage battery, nickel oxide, NiO, is changed to metallic nickel at one electrode, in discharging the cell. Is this electrode anode or cathode? In the reverse reaction, in charging the cell, is it anode or cathode?

15. Write electronic equations showing gain or loss of electrons in the reactions of the three preceding questions, representing salts of any given metal by the formula of the metallic ion.

16. Write an electronic equation to show what happens when a ferric salt is converted into a ferrous salt. Also when a mercurous salt, Hg_2^{++}, is converted into a mercuric salt, Hg^{++}.

17. Write and balance an electronic equation in which a sulfite, SO_3^{--}, serves as a reductant and is oxidized to a sulfate.

18. Write and balance an electronic equation for a reaction in which arsenic trioxide, As_2O_3, is converted into an arsenate, AsO_4^{---}. (Make sure that arsenic balances, as well as oxygen.)

19. Show that oxygen in hydrogen peroxide and nitrogen in nitrite ion actually have the valence numbers stated.

20. Write and balance an electronic equation for the reduction of nitric acid to nitric oxide.

21. Write and balance an electronic equation for the reduction of a permanganate, MnO_4^-, to a manganous salt, Mn^{++}.

22. Write and balance an electronic equation for the reduction of an iodate to an iodide.

23. Write and balance an electronic equation for the reduction of a nitrate to nitrous oxide, N_2O.

24. Combine electronic equations in Exercises 17 and 20 to obtain a balanced ionic equation for the oxidation of a sulfite by nitric acid.

25. Combine electronic equations in Exercises 18 and 22 to obtain a balanced ionic equation for the oxidation of arsenic trioxide by an iodate.

26. Combine electronic equations in Exercises 17 and 21 to obtain a balanced ionic equation for the oxidation of a sulfite by a permanganate.

27. Rewrite equations in Exercises 24, 25, and 26 as valence state equations.

28. By reference to the table of oxidation potentials (§ 267) determine which of the following reactions may be expected to take place, and in which the reverse reaction is indicated:

A stannous salt is to reduce a ferric salt to a ferrous salt.
Metallic zinc is to reduce a chlorate to a chloride.
A ferric salt is to oxidize a manganous salt to a permanganate.
A permanganate is to oxidize a stannous salt to a stannic salt.

Chapter 21

THE HALOGENS

(Column 7A of the Periodic Table)

Symbol	Atomic Number		Formula	Melting Point(°C)	Boiling Point(°C)
F	9	Fluorine—pale yellow gas	F_2	$-223°$	$-188.2°$
Cl	17	Chlorine—greenish yellow gas	Cl_2	$-103°$	$-34.7°$
Br	35	Bromine—dark red liquid	Br_2	$-7.2°$	$58.0°$
I	53	Iodine—purplish black solid	I_2	$113.0°$	$183.0°$
	85	A synthetic element, probably not existing in nature, because unstable)	....	....	....

269. Occurrence of the Halogens

The halogens (*Greek:* salt formers) receive their name from their occurrence as common salt and related compounds, in sea water. They are *typical non-metals*, so active chemically that they are never found free in nature.

Fluorine differs from the other halogens in forming an insoluble calcium salt, *fluorspar*, CaF_2. This is widely distributed as minute crystals in *igneous rocks*. Fluorine also occurs as *cryolite*, Na_3AlF_6 (an aluminum ore, § 541). An important mineral, widely distributed, is the double salt *apatite*, which is calcium phosphate-fluoride, $Ca_5(PO_4)_3F$ (§ 384). Calcium fluoride is present in the enamel of teeth, and traces of dissolved fluorides are present in sea water and are sometimes detectable in ordinary drinking water. (Ex. 1, 2.)

Bromine occurs as soluble bromides in sea water, in sufficient quantity to yield a pound of bromine to every $7\frac{1}{2}$ tons of water. This is hardly $\frac{1}{300}$ of the content of chlorine in sea water. Nevertheless bromine can be economically recovered from sea water (§ 278). When the brine from certain salt wells in Michigan and elsewhere is partially evaporated to recover common salt, the remaining mother liquor contains a sufficient quantity of sodium bromide to serve as a commercial source of bromine.

Iodine occurs in sea water in mere traces—about 1 part in 20,000,000—as soluble iodides, which are removed from the water in

the growth of seaweed (kelp) and accumulated in the tissues of these plants. The ash of kelp was long the chief commercial source of iodine. At present, iodine is chiefly obtained from sodium iodate, $NaIO_3$, which occurs to the extent of about 0.2 per cent as an impurity in the sodium nitrate beds of Chile. Brines encountered in petroleum wells along the coast of Southern California contain about 70 parts of iodine per million, and now supply much of the iodine used in the United States. (Ex. 3, 4.)

270. Valence States of the Halogens

The chief reactions of the halogens are summarized in the following table. Dashes in the table indicate that certain of the higher valence states of fluorine and the valence state +7 for bromine are unknown. Numbers accompanying the arrows in the table refer to equations in the next few pages, numbered to agree with corresponding equations in the chapter on chlorine (§§ 196–207). The present chapter will serve as a review of the chemistry of chlorine, with emphasis on transfers of electrons that occur when the halogens and their compounds serve as oxidizing agents.

Valence Number	Examples				General Formula
−1	F^- HF	Cl^- HCl	Br^- HBr	I^- HI	X^- $\underset{2}{\rightleftarrows}$ HX
0	F_2	Cl_2	Br_2	I_2	X_2
+1	F_2O (unimportant)	Cl_2O or ClO^-	BrO^-	IO^-	$HXO \underset{17}{\leftrightarrows} XO^-$
+3	—	$HClO_2$ Chlorous acid (unimportant)	—		
+4	—	ClO_2	—	IO_2	
+5	—	$HClO_3$ or ClO_3^- Chloric acid, Chlorate-ion	BrO_3^- Bromate-ion	IO_3^- or I_2O_5 Iodate-ion	XO_3^- Halate-ion
+7	—	Cl_2O_7, $HClO_4$ or ClO_4^-	—	IO_4^-	$HXO_4 \xleftarrow{27} XO_4^-$ Perhalate-ion

The student should make an earnest effort to become acquainted with all the reactions shown in this table. Those not found in the present chapter should be sought under the same number in the chapter on chlorine.

271. Preparation of the Hydrogen Halides

1. The hydrogen halides (HF, HCl, HBr, HI) are usually prepared by heating a halide salt with a *non-volatile, non-oxidizing* acid. Representing the halide ion (*i.e., any halide*) by X^-, the general equation for the preparation of a hydrogen halide is:

Equation 1: $$X^- + H^+ \rightarrow \underset{\text{Hydrogen halide}}{HX} \uparrow$$

Specifying a particular salt and a particular acid we may write:

$$NaX + H_2SO_4 \rightarrow NaHSO_4 + HX \uparrow$$

Concentrated sulfuric acid should be used in preparing HF and HCl; but somewhat diluted acid must be used in the preparation of HBr, else the HBr will be oxidized by the sulfuric acid, forming water and bromine. Use phosphoric acid instead of sulfuric in the preparation of HI, because HI is very readily oxidized (in other words, is a very vigorous reducing agent). (Ex. 5.)

2. The hydrogen halides may also be prepared by direct union of hydrogen with the halogens (§ 277).

272. Properties of the Hydrogen Halides and Hydrohalogen Acids

The hydrogen halides are all colorless gases with a sharp odor. They are very soluble in water (forming solutions of the hydrohalogen acids):

Equation 2: $$H_2O + HX \xrightarrow{H^+} \underbrace{H_3O^+ + X^-}_{\text{Hydrohalogen acid}}$$

This reaction accounts for the heavy fumes (microscopic droplets of liquid) that are formed when the hydrogen halides come in contact with moist air.

Hydrofluoric acid, in contrast with other hydrohalogen acids, is but slightly active. This is due chiefly to the fact that the fluoride ion has so small a radius (table, § 273) that a proton may approach it very closely and be firmly bound.

Hydrogen fluoride differs from the other hydrogen halides in being strongly associated (§ 123) at low temperatures, forming molecules of the formula H_6F_6. The proportion of associated molecules decreases with increasing temperature, and at room temperature is such as to give an average molecular weight of about 50. At about 90°C dissociation into the simple molecules, HF, is complete. (Ex. 6.)

The tendency toward association is another result of the small radius of the fluorine atom or ion. This enables two fluorine atoms to approach each other closely and imprison a proton between them—an example of a *hydrogen bond*. Thus one may obtain $H:\ddot{\underset{\cdot\cdot}{F}}:H:\ddot{\underset{\cdot\cdot}{F}}:$ or even H_6F_6 (with six simple HF molecules linked in a chain or ring). Associated molecules of this sort, by loss of one or more protons, become acid fluoride ions, such as $\left[:\ddot{\underset{\cdot\cdot}{F}}:H:\ddot{\underset{\cdot\cdot}{F}}:\right]^-$. Thus we account for the formation of *acid fluorides*, such as $KF \cdot HF$ and $KF \cdot 3HF$. The other hydrohalogen acids show no such tendency.

In spite of slight activity, strong solutions of hydrofluoric acid produce serious and painful burns, best treated by *immediate washing with ice water*, continued for at least half an hour.

Hydrofluoric acid is distinguished by its ability to etch glass. This property is due in part to the fact that the reaction happens to form a volatile product:

$$\underset{\text{(A component of glass)}}{SiO_2} + 4HF \rightarrow \underset{\text{Silicon fluoride (gas)}}{SiF_4\uparrow} + 2H_2O$$

The reaction also produces a certain quantity of another gas, hydrogen fluosilicate, H_2SiF_6.

The hydrohalogen acids are typical *active acids* in reacting with metals, metallic oxides, alkalies, carbonates, sulfites, and sulfides as already described in §§ 184, 191. Expressed as ionic equations:

Equations 3:

$$O^{--} + 2H^+ \rightarrow H_2O$$

$$OH^- + H^+ \rightarrow H_2O$$

$$S^{--} + 2H^+ \rightarrow H_2S\uparrow$$

$$CO_3^{--} + 2H^+ \rightarrow CO_2\uparrow + H_2O$$

$$SO_3^{--} + 2H^+ \rightarrow SO_2\uparrow + H_2O$$

The other product, in each reaction, is a *halide salt*. (Ex. 7.)

All the hydrogen halides form heavy white fumes (microscopic crystals of halide salt) when reacting with ammonia gas, as already described for hydrogen chloride (§ 186):

$$\underbrace{NH_3 + HX}_{H^+} \rightarrow \underbrace{NH_4^+ + X^-}_{\text{Ammonium halide}}$$

273. Oxidation of the Halide Ions

Let us arrange the halide ions in the order of increasing atomic number:

Atomic number:	9	17	35	53
	F^-	Cl^-	Br^-	I^-
Ionic radius:	1.31	1.81	2.00	2.20×10^{-8} cm

The outermost electrons are relatively close to the nucleus in the fluoride ion, F^-, and are strongly held by the positive charge on the nucleus, whereas they are further and further removed from the nucleus and less and less strongly held with increasing ionic radius. The fluoride ion actually holds its surplus electron so strongly that no known oxidizing agent will remove it. The iodide ion, by contrast, readily loses its surplus electron, hence serves as a reductant (§ 261).

274. Preparation of the Halogens

The free halogens are always prepared by oxidizing the corresponding halide ion, that is, *by causing a halide ion to part with an electron,* which is either transferred (1) to some oxidizing agent or (2) to the anode (in electrolysis):

Equation 4: $$X^- \rightarrow \tfrac{1}{2}X_2 + e$$

in which X^- represents any halide (fluoride, chloride, bromide, or iodide), and X_2 represents any free halogen.

To prepare elementary fluorine we must resort to electrolysis and compel the fluoride ion to yield an electron at the anode (§ 260):

$$F^- \rightarrow \tfrac{1}{2}F_2 + e$$

Apparatus found convenient (*J. Am. Chem. Soc.* **60,** 96 [1938]) for preparing fluorine is shown in Fig. 103. The electrodes are graphite, and the electrolyte is fused potassium acid fluoride, KF·3HF, contained in a V-shaped copper vessel. Electrolysis takes place at 70 to 100°C. After a preliminary period in which traces of water in the electrolyte are decomposed by electrolysis, fluorine is produced freely.

It may be recognized by its ozone-like odor and by the fact that it will set fire to a gas jet brought near the exit tube leading from the anode. At the cathode, gaseous hydrogen is evolved. (Ex. 8.) The electrodes need to be sandpapered after the preliminary electrolysis and occasionally thereafter, to remove a coating of silica that gradually accumulates.

The preparation of chlorine by the electrolytic oxidation of a chloride (§ 198), or by the oxidation of hydrogen chloride with manganese dioxide or some other vigorous oxidant (§ 263), has already been described. A dichromate or permanganate is often employed. (Ex. 9.)

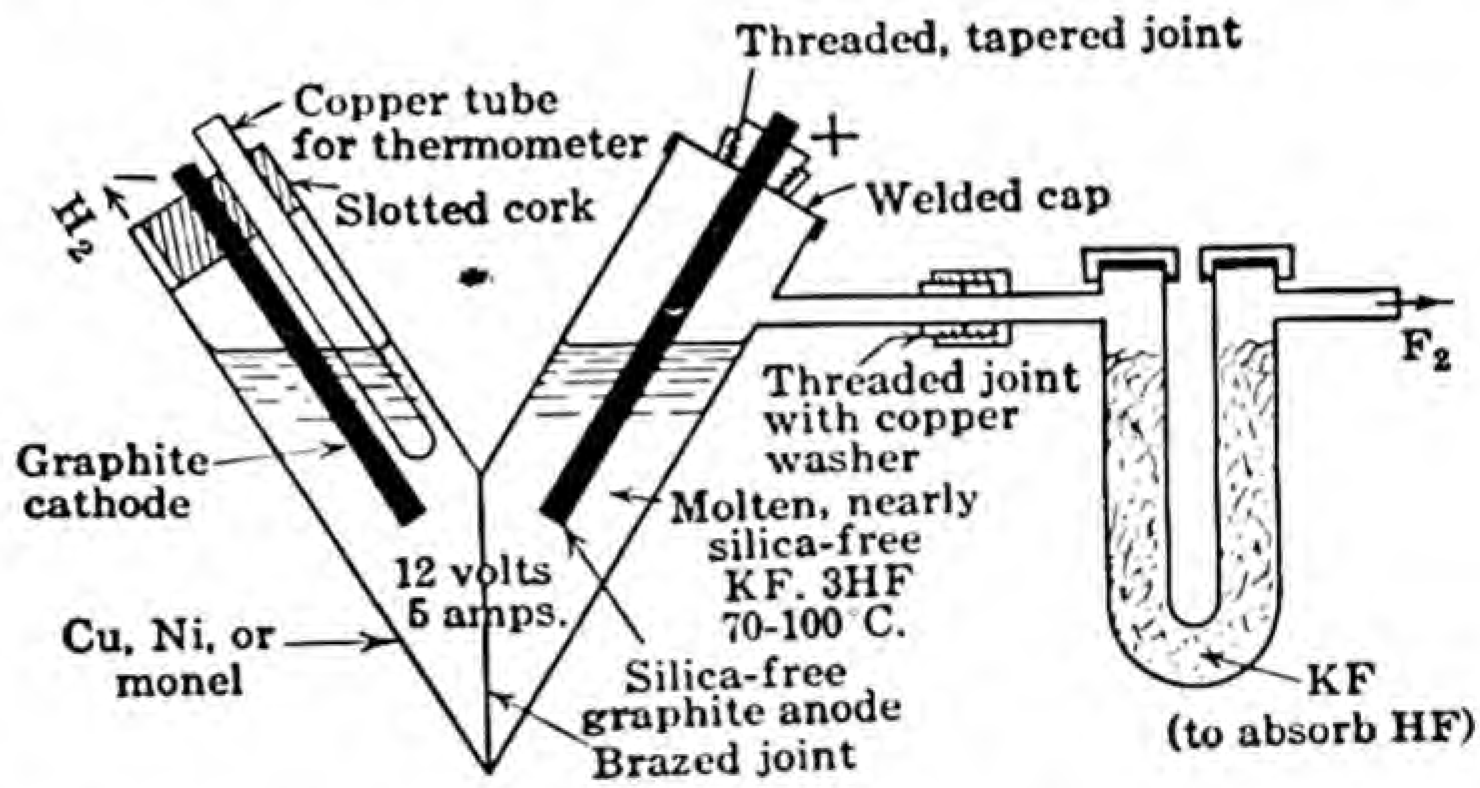


FIG. 103. Preparation of fluorine. The electrolyte may be kept molten by a small flame or by a current through resistance wire, wound around the cell, over a layer of asbestos paper.

In the preparation of bromine or iodine by the oxidation of a bromide or an iodide (including hydrogen bromide and hydrogen iodide), the procedure is the same as in the preparation of chlorine, except that less vigorous oxidants may be used, including chlorine itself (in preparing bromine and iodine) and bromine itself (in preparing iodine), as described in § 278.

275. Physical Properties of the Halogens

Some of the more important physical properties of the halogens are indicated in the table at the head of this chapter (p. 318). Observe the gradual transition with increasing atomic number, hence increasing atomic radius, from a difficultly condensable gas (F_2) to a readily condensable gas (Cl_2), a liquid (Br_2), and a solid (I_2). This indicates that with increasing atomic radius the outermost electrons in each atom get farther and farther from the nucleus and so exert more force upon neighboring molecules, tending first toward liquefaction then toward giving the molecules a definite arrangement in the crystal lattice of a solid. Examination with X-rays (§ 140) reveals that even in

the solid state the halogens possess diatomic molecules, as may be demonstrated for the gaseous state or vapor state by the fact that 22.4 liters of the gas or vapor, recalculated to standard conditions, weigh twice the gram-atomic weight.[1]

The gradual increase in color as we pass from fluorine (yellow) to chlorine (yellow-green), bromine (dark red), and iodine (purplish black) is in part due to the change of state (liquid chlorine, for example, is a deep orange color, as compared with greenish yellow for gaseous chlorine). The rest of the darkening is due to an increase in atomic mass and atomic radius.

276. Chemical Properties of the Halogens

Atomic number:		9	17	35	53
		F_2	Cl_2	Br_2	I_2
Electrons:	*K*	2	2	2	2
	L	7	8	8	8
	M		7	18	18
	N			7	18
	O				7
Electron affinity:		4.13	3.75	3.53	3.22 volts

The most important chemical properties of the halogens depend on the tendency of every halogen atom (7 valence electrons) to complete its outer octet either (1) by gaining an electron from some other atom, thus forming a *halide ion*, X^-; or (2) by gaining a share in a pair of electrons, thus becoming linked to another atom by a *covalent bond* (§ 244). But since the atom that is compelled to yield an electron or a share in electrons is thereby oxidized, the halogens, in all their important reactions, are active *oxidants*.

This tendency of a monatomic neutral particle (F, Cl, etc.) to gain electrons is measured by the *electron affinity*, in volts. It is *greatest for the fluorine atom*, since its small radius enables the added electron to approach the positively charged nucleus very closely and be strongly held. *The tendency diminishes with increasing atomic radius and is least for the iodine atom.* The converse tendency, namely for halide ion to lose an electron, is greatest for I^- and least for F^-, as we have already seen (§ 273).

[1] We may also note that when a gaseous halogen combines with hydrogen to form a hydrogen halide, HX, the volume of the gaseous product, hence the number of molecules contained in it, is twice that of the original halogen. Each molecule of free halogen must therefore be divisible by 2, and the simplest assumption is that it has the formula X_2.

The tendency of halogen atoms to share electrons (forming a covalent bond) results in their sharing electrons among themselves, to form not only diatomic molecules, F_2, etc., in which both atoms are alike, but also *interhalogen compounds*, such as ICl, BrCl, ClF. A large atom may also coordinate 3, 5, or perhaps even 7 smaller atoms, as in ICl_3, IF_5, IF_7. The large radius of the iodine atom is probably responsible for its forming the triiodide ion, I_3^-. In consequence, *iodine dissolves freely in solutions of soluble iodides*, forming a deep brown solution:

$$I_2 + I^- \rightarrow \underset{\text{(Dissolved)}}{I_3^-}$$

277. Direct Union of the Halogens with Other Elements

In the direct union of the halogens with hydrogen the two elements become linked by a pair of electrons (a covalent bond):

Equation 7: $$H_2 + X_2 \rightarrow 2HX$$

Hydrogen and *fluorine* combine with explosive violence, even when solid fluorine, below $-223°C$, is brought into contact with hydrogen, in the dark.[2] The direct union of hydrogen and *chlorine* takes place explosively in the sunlight (§ 200). The direct union of hydrogen and *bromine* is reversible and therefore incomplete, though sufficiently rapid to serve as a commercial method for the preparation of hydrogen bromide when the two reactants are passed over a catalyst of heated charcoal. The direct union of hydrogen and *iodine* is still less nearly complete, the yield of hydrogen iodide becoming less as the temperature is raised.

The direct union of the halogens with other elements to form covalent compounds, in which the atoms are linked by pairs of shared electrons, is shown in the formation of $SbCl_3$, Al_2Cl_6, S_2Cl_2, SCl_4, PCl_3, and PCl_5 (Equations 8 to 10, § 200). An interesting compound of this type is sulfur hexafluoride, SF_6, in which the relatively large size of the sulfur atom enables it to make contact with and combine with six fluorine atoms (a coordination number of 6, § 253). The sulfur atom then shares twelve electrons with the six surrounding fluorine atoms.

The halogens react with hydrocarbons and many other classes of organic compounds to form thousands of different compounds (1) by direct addition or (2) by *substitution* (Equations 12 and 13, § 202). Iodine is distinctly less active than the other halogens and sometimes

[2] The reaction fails to take place in capillary glass tubes or in old glass vessels, perhaps because SiF_4 acts as a negative catalyst.

fails to react with organic compounds when bromine and chlorine do so quite readily. The reactions of fluorine with organic compounds have not been very completely investigated.

278. Displacement of One Halogen by Another

Review § 276. In a contest for electrons between the atoms of two different halogens, the halogen of smaller radius of course wins, combining with an electron and setting free the atom of larger radius:

Equation 11: $\frac{1}{2}Cl_2 + Br^- \rightarrow Cl^- + \frac{1}{2}Br_2$

In this manner bromine is produced commercially from bromides, for example, from the traces of bromides present in sea water. In this reaction chlorine gains an electron from bromide ion, releasing free bromine. Turn to § 201 for conventional equations for reactions in which the chlorine displaces bromine from NaBr, $CaBr_2$, and Al_2Br_6.

Chlorine is used to displace bromine from sea water in the presence of dilute sulfuric acid, which tends to prevent loss of bromine in formation of hydrobromic and hypobromous acids (Equation 14, next following).

279. Reaction of the Halogens with Alkalies and Soluble Carbonates

Fluorine reacts with water to form hydrofluoric acid and ozonized oxygen. For this reason fluorine cannot be employed as a reagent in the presence of water, as is often done with the other halogens.

The reaction of chlorine or bromine with water (§ 203) may be written:

Equation 14: $$2H_2O + X_2 \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \underbrace{H_3O^+ + X^-}_{\substack{\text{Hydrochloric} \\ \text{(or hydrobromic)} \\ \text{acid}}} + \underset{\substack{\text{Hypochlorous} \\ \text{(or hypobromous)} \\ \text{acid}}}{HOX}$$

if we wish to emphasize that hydrochloric acid differs from hypochlorous acid (a slightly active acid) in being completely ionized. The reaction of bromine with water is still less nearly complete, and that of purified iodine is barely detectable.

In the presence of acid the left-to-right reaction (*a*) in the preceding equilibrium is almost prevented. In the presence of an alkali or soluble carbonate, to neutralize and so remove the acid produced as fast as it is formed, the right-to-left reaction (*b*), in the equilibrium just formulated, is prevented, hence the left-to-right reaction (*a*) becomes complete:

Equation 15: $2OH^- + X_2 \rightarrow \underset{\text{Hypohalite ion}}{XO^-} + \underset{\text{Halide ion}}{X^-} + H_2O$

Equation 16: $CO_3^{--} + X_2 \rightarrow XO^- + X^- + CO_2\uparrow$

The solution must be kept cold; otherwise the hypohalite is converted into halate. This change takes place very readily with *hypoiodites*, even in cold solutions:

Equation 21: $3XO^- \rightarrow 2X^- + XO_3^-$

By the reaction of a halogen with a hot solution of an alkali or soluble carbonate a *halate* (chlorate, bromate, or iodate) is produced directly:

Equations 22: $6OH^- + 3X_2 \rightarrow 5X^- + XO_3^- + 3H_2O$

$$3CO_3^{--} + 3X_2 \rightarrow 5X^- + XO_3^- + 3CO_2\uparrow$$

(Ex. 10.)

280. Oxyhalogen Salts and Acids

The preparation and properties of *hypochlorites* have been discussed in § 204. *Hypobromites* are like hypochlorites. Both are stable in alkaline solution and then serve as useful oxidizing agents, being reduced to chlorides or bromides:

$$BrO^- + 2H^+ + 2e \rightarrow Br^- + H_2O$$

As a valence state equation (§ 266) this would be written:

$$Br^{+1} + 2e \rightarrow Br^-$$

Chlorates and *perchlorates* are discussed in §§ 206, 207. The *corresponding bromine and iodine compounds* are of similar properties. A mixture of bromate and bromide is *a useful laboratory source of free bromine*, needing only to be acidified with dilute sulfuric acid and distilled:

Equation 23: $BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2\uparrow + 3H_2O\uparrow$

Bromates are useful oxidizing agents in strongly acid solutions, being reduced to bromide, in most instances:

$$BrO_3^- + 6H^+ + 6e \rightarrow Br^- + 3H_2O$$

As a valence state equation this would be written:

$$Br^{+5} + 6e \rightarrow Br^-$$

(Ex. 11.)

Iodates are salts of iodic acid, HIO_3, which may best be prepared by direct oxidation of iodine by concentrated nitric acid or by chlorine in the presence of moisture. It is a deliquescent, extremely soluble, crystalline solid, which is a powerful oxidizing agent. When iodic acid is gently heated it loses water and is converted into a white solid, iodine pentoxide, I_2O_5. This has often been used in gas masks specially designed to oxidize and remove carbon monoxide.

Fluorine forms several oxides, but oxyfluorine salts are unknown.

281. Uses of the Halogens

The extreme chemical activity of *fluorine* has made it difficult to study and apply commercially.

All fluorides are intensely poisonous. Lithium and sodium fluorides are used as a flux in soldering aluminum, and for impregnating wood to preserve it from destruction by fungi. Ammonium fluoride is sometimes used for disinfecting vessels in the brewing and dairy industries. Several fluorine-substituted hydrocarbons serve as the working fluid in domestic refrigerators, largely replacing sulfur dioxide and other substances formerly used. The most important examples are CCl_2F_2 (Freon) and $CHFCl_2$. Such compounds are usually prepared by treating the corresponding chlorine compounds with hydrogen fluoride or a metallic fluoride in the presence of a catalyst (for example, $SbCl_5$). (Ex. 12.)

The uses of elementary *chlorine* have been described in § 208. Those of the hypochlorites, chlorates, and perchlorates will be found in §§ 204, 206, 207.

The chief use of *bromine*, in the United States, is in the preparation of ethylene dibromide, $C_2H_4Br_2$, as an ingredient of ethyl gasoline. Bromine is used to some extent as a substitute for chlorine, in the disinfection of water supplies. It is used in the preparation of hypobromites, bromates, and certain dyestuffs.

Bromides, in medicine, serve as heart depressants and nerve sedatives. Silver bromide suspensions (with a little silver iodide) are used for coating photographic plates and films (§ 569). (Ex. 13.)

Iodine is familiar to all as a household disinfectant, in the form of *tincture of iodine*, which is a solution of iodine and potassium iodide in alcohol. Some of the organic compounds of iodine are important drugs and dyes. *Iodoform*, CHI_3 (a yellow crystalline powder with a characteristic odor), and several other iodine compounds are useful as disinfectants.

It has long been known that the animal body contains small amounts of chemically combined iodine, and that iodine, in traces, is a necessary ingredient of the diet. The human body contains about 12 mg of iodine, most of which is localized in the thyroid gland, at the base of the neck. The iodine of the thyroid gland exists as an organic compound called *thyroxin*, which has been synthesized in the laboratory. It is one of the group of organic compounds called *hormones*, which control the processes of life, and thus, in a very real sense, determine our destiny (§ 478).

282. Tests for the Halogens

Silver fluoride is soluble. The silver halide salts of the other halogens are insoluble. Accordingly, a *chloride*, *bromide*, or *iodide* may be detected in an acidified solution by the addition of a silver salt:

$$Ag^+ + Cl^- \rightarrow AgCl \downarrow$$

The identity of the halide thus precipitated may be judged by the color of the precipitate. Silver chloride is white, silver bromide pale yellow, and silver iodide lemon yellow. Silver chloride and bromide may also be distinguished from silver iodide by the fact that they dissolve in ammonium hydroxide solution, forming complex salts called *ammines* (§ 364). (Ex. 14.)

Traces of *bromide* or *iodide* may also be detected by adding a few drops of a solution of free chlorine, then shaking the solution with a few drops of some organic solvent immiscible with water (carbon tetrachloride, chloroform, ether, carbon disulfide). The halogens are much more soluble in these solvents than in water, and are therefore extracted by the solvent chosen, until the concentration in the solvent, at any given temperature, is some definite large multiple of the concentration in the water. *Bromine*, in organic solvents, usually has a yellow-brown or amber color. *Iodine*, in most solvents, appears of a purplish or lilac shade; but, in ether, alcohol, and other solvents containing oxygen, it usually forms yellow to brown solutions, depending on the concentration.

If *both bromide and iodide* are present in a solution, a limited amount of chlorine will liberate iodine first and permit it to be recognized in the presence of a very large amount of bromide. Other methods of separating bromine and iodine depend on the fact that iodine may readily be oxidized to iodic acid, whereas it is difficult to oxidize bromine to bromic acid.

Traces of iodine are readily recognized by the blue color that it gives to starch. This test is so delicate that one part of iodine in several million parts of water may readily be detected. It may also be used to detect minute traces of free chlorine or bromine, or indeed of any substance capable of liberating iodine from an iodide. (Ex. 15.) The blue color is not a definite compound, but an optical effect obtained when iodine is adsorbed by various materials.

For a review of this chapter refer to Exercises 16–30.

Technical Words

Igneous rocks (a geological term)—rocks that have been formed by the slow or rapid cooling of molten material. By contrast, **sedimentary rocks** are formed by deposition of material carried in suspension by running water or produced by marine organisms; and **metamorphic rocks** are formed by alteration of rocks of the two preceding classes, through the agency of heat and pressure.

Double salt, p. 318. **Complex salt,** p. 656.

Tincture—a pharmaceutical term, referring to a solution of some drug or medicinal substance in ethyl alcohol.

Hormone, p. 329.

Exercises

1. If the cation in cryolite is Na^+, what must be the anion?

2. What ions are present in apatite? Explain (§ 145) how double salts come to be formed and why cryolite is not regarded as a double salt.

3. If sodium nitrate contains, as an impurity, 0.2 per cent of sodium iodate, what percentage of iodine does it contain? 128

4. If a brine contains 70 parts iodine per million, how many tons of brine are needed to yield 1 lb of potassium iodide (1 ton = 2000 lb)? 714

5. Write an equation for the preparation of hydrogen iodide by treating sodium iodide with phosphoric acid, assuming that only one of the hydrogen atoms in phosphoric acid is replaced by sodium.

6. About how does the density of hydrogen fluoride, at room temperature and at 90°C, compare with that of air at the same temperature? 172, 690

7. What volume of carbon dioxide, under standard conditions, is evolved for each millimole of carbonate, when treated with an acid? 224

8. Write an electronic equation for the reaction occurring at the cathode in the electrolysis of molten potassium acid fluoride.

9. Write electronic equations (§ 262) for the oxidation of a chloride to chlorine, the oxidizing agent being dichromate ion, which is thereby reduced to chromic ion, Cr^{+++}.

Combine these two equations to obtain a balanced ionic equation.

10. Write and balance an equation for the preparation of sodium iodate from sodium carbonate. What fraction of the iodine used is actually converted into iodate in this reaction?

11. Write an electronic equation for the oxidation of arsenic trioxide, As_2O_3, to arsenic acid, H_3AsO_4. Combine this with an electronic equation in the text, to obtain a balanced ionic equation for the oxidation of arsenic trioxide by a bromate.

12. Estimate the weight of 1 liter of gaseous Freon (§ 281), under standard conditions. 540

13. What volume of ethylene gas, C_2H_4, under standard conditions, is needed to produce 1 kg of ethylene dibromide? 118

14. Write an equation for the reaction of silver bromide with ammonium hydroxide solution, to form a complex salt, containing the ions $Ag(NH_3)_2^+$ and Br^-.

15. What products result when hydrogen peroxide (§ 263) reacts with an iodide? Write a balanced ionic equation.

16. Write the name and formula of a fluorine mineral that is a complex salt and of one that is merely a double salt. What is the difference between these two classes of salts?

17. Write equations for simple methods for preparing the substances that follow sodium bromide in the following list, deriving *each from the preceding one*: sodium bromide, hydrogen bromide, hydrobromic acid, calcium bromide (together with carbon dioxide gas), free bromine, potassium hypobromite, potassium bromate, potassium bromide, silver bromide.

18. Write an equation for the method commonly used to displace bromine from sea water. Explain why several pounds of sulfuric acid are commonly added to each ton of sea water before adding chlorine to displace bromine.

19. Bromine displaced from sea water is usually removed by a current of air and absorbed in a solution of sodium carbonate. Give an equation for the reaction that takes place, assuming that the solution may become warm during the reaction.

20. How may the hydrogen halides be prepared (1) from a halide salt; (2) from the free halogen?

21. How may hypochlorites and hypobromites be prepared?

22. What is the most important property of hypochlorites and hypobromites? Under what conditions are these compounds fairly stable?

23. How are elementary chlorine and bromine prepared? Illustrate by an equation, using some particular salt, then give the corresponding ionic equation, and finally a valence state equation.

24. What is the principal use of bromates in the laboratory? Illustrate by an electronic equation, then give the corresponding valence state equation.

25. Which of the halogens is the most vigorous oxidant? How do we account for this fact?

26. What is meant by oxidation potential? What happens to the oxidation potential of the halide ions, with increasing ionic radius? Which halide ion is therefore classed as an active reductant?

27. What are the chief uses of the free halogens?

28. What class of gaseous fluorine compounds is important in industry? What are the chief industrial uses of fluorides?

29. Tell something of the importance of iodine in the animal body.

30. Explain how one may determine whether a given solution contains only a chloride, a mixture of chloride and bromide, or perhaps a mixture of bromide and iodide.

Chapter 22

SOLUTIONS

283. Different Kinds of Dispersions

A *dispersion* is a mixture produced by subdividing one material and scattering its particles through another. Sometimes the dispersed particles are large enough to be visible to the eye, or under the microscope. In muddy water, the dispersed particles are visible or microscopic particles of clay. In milk they are microscopic droplets of butterfat.

When the dispersed particles are of less than microscopic size, yet still enormous in comparison with ordinary molecules, we have what is termed a *colloidal dispersion*, less properly termed a colloidal solution. Colloidal dispersions are so important that we shall presently devote an entire chapter to a discussion of their properties (§§ 428–439).

When the dispersed particles are the actual *molecules or ions* of which the dispersed substance is composed, we have a *molecular dispersion*, more commonly called a *solution*. A solution may otherwise be defined as a completely homogeneous mixture. Its *composition* and *properties* are always capable of being varied by imperceptible degrees (within certain limits of composition), simply by varying the proportions in which its components are present.

For example, a solution of sugar in water appears to be perfectly homogeneous, even when examined under the most powerful microscope. Furthermore, such a solution may vary continuously, in composition and properties, from nearly pure water, perhaps just detectably sweet, to a strong sugar sirup from which crystals slowly separate.

Solutions may be gaseous, liquid, or solid. The important thing is that the mixture shall be *homogeneous by all tests* and that *its composition and properties shall be capable of variation by imperceptible degrees.* Any mixture of gases is entitled to be called a *gaseous solution;* and glass, many alloys (for example, ordinary 18-carat gold), and many homogeneous rocks and minerals are examples of *solid solutions.*

Many of the most interesting and important things in nature have to do with solutions. A liquid solution, the ocean, covers three fourths

of the earth's surface. The air we breathe is a gaseous solution. Solutions carry mineral foods from the roots of plants to the topmost branches, and return with other materials, to be stored up as woody tissue, starch, or sugar, in stem, or leaves, or tubers. They carry out our digestive processes; they course through our veins; they form the fluid contents of every living cell. In brief, the whole aspect of our earth, and all the forms of life that exist upon its surface, are determined by the properties of solutions.

284. Solvent and Solute

At least two materials are contained in every solution. The material that *dissolves* the other, and so comes to form a continuous medium, surrounding the dispersed molecules of the other, is called the *solvent*. An *aqueous solution* is one in which the solvent is water. The material that is dispersed as separate molecules or ions, scattered through the solvent, is called the *solute*.[1]

When two or more substances intermingle to form a homogeneous solution *in whatever proportions they are brought together*, they are said to be *miscible* in all proportions, or to be *completely miscible*. Water and alcohol furnish an example. We may pass gradually and continuously from a very dilute solution of alcohol, in water as a solvent, through solutions that contain more and more alcohol, to those that are nearly pure alcohol, serving as solvent for a very little water.

When two materials are completely miscible the component that happens to make up most of the mixture may fairly be regarded as the *solvent;* but when the two are present in nearly equal proportions no distinction may be made between solvent and solute.

285. Polar and Non-Polar Substances

Even in an electrically neutral molecule, opposite ends sometimes carry opposite electrical charges. For example, the two particles H and Cl, in gaseous hydrogen chloride, HCl, are linked together to form a molecule, the hydrogen end of which appears to carry a positive charge and the chlorine end a negative charge. Such a molecule is called a *polar molecule*, or a *dipole molecule*. Substances possessing such molecules are sometimes called *polar substances*. The same term is often applied to what we have termed ionic substances, though these really represent substances in which the oppositely charged poles have become separated.

[1] Pronounced *sŏl-ūte'*.

A completely non-polar molecule is obtained only when the molecule has a *symmetrical structure*, as when two atoms of the same element combine (examples: Cl—Cl, O═O, N≡N). Molecules that depart widely from a symmetrical structure (examples: H—Cl, $\mathrm{H{-}\ddot{O}\!:}$ with H below the O, $\mathrm{H{-}\ddot{N}{-}H}$ with H below the N) are polar.

Polar molecules, when placed between two oppositely charged plates, tend to orient themselves, with the positive end of each molecule directed toward the negative plate, and conversely (Fig. 104). Naturally, the confused and irregular motion of the molecules prevents this orientation from being anywhere nearly perfect or complete, and such orientation as does occur of course diminishes with increasing temperature.

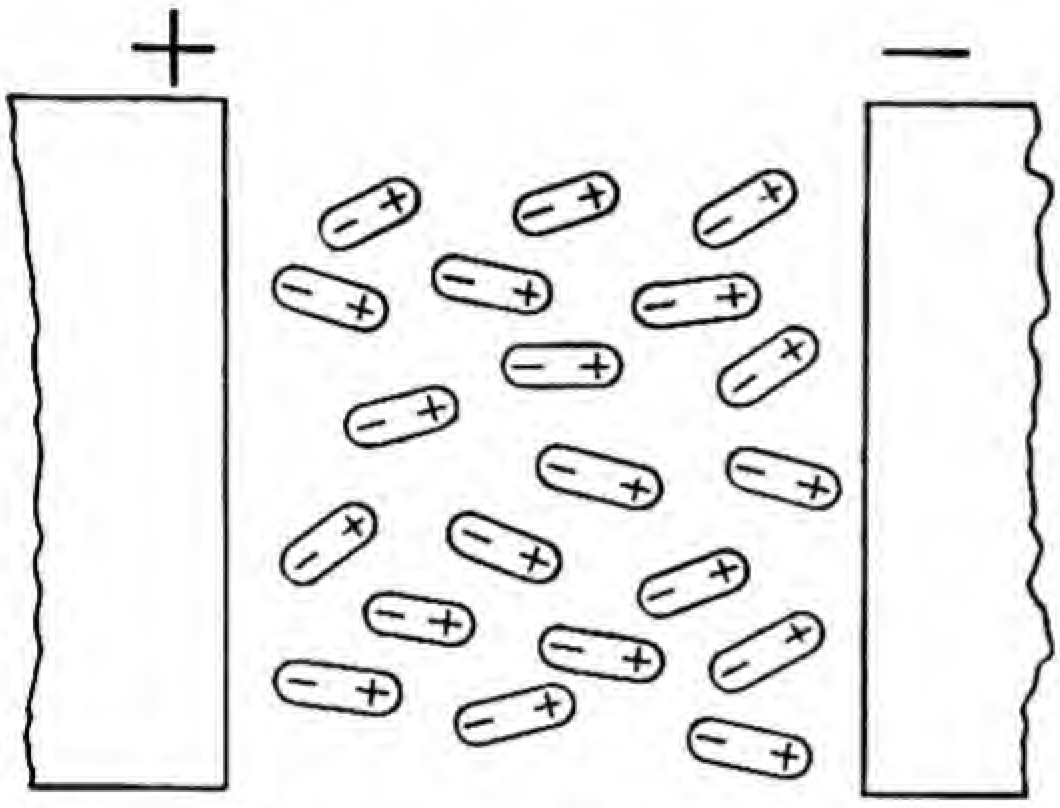


FIG. 104. Orientation of polar molecules in an electrostatic field.

The tendency of molecules thus to orient themselves in an electric field is measured by what is called the *dipole moment* of the substance, which is closely related to its *dielectric constant* (defined on p. 348). When the dielectric constant of a substance does not exceed 4 units the substance may be regarded as practically non-polar.

DIELECTRIC CONSTANTS (20°C)

Acetic acid	9.7	Carbon disulfide	2.6
Acetone (0°C)	26.6	Chloroform	5.2
Alcohol (ethyl)	25.8	Carbon tetrachloride	2.24
Alcohol (methyl)	35.0	Ethyl ether	4.3
Ammonia (−34°C)	21–23	Hydrogen peroxide (46%)	84.7
Benzene	2.3	Petroleum	2.1
Bromine	3.18	Water	81.0

Polar substances manifest their polar nature not only (1) by *high dipole moment* or *high dielectric constant*, but also (2) by being *chemically reactive*. The molecules of such a substance, because of their being reactive, combine with one another (association, § 123). This results in (3) *high heat of vaporization*, and also (4) *high surface tension*. So here are four different tests by which a polar substance may readily be recognized.

By all four tests, both water and ammonia are revealed as highly polar substances, which are strongly associated in the liquid state. By linking simple molecules together, through intervening protons, water and ammonia build up associated molecules of indefinite size (§ 250), which are constantly being added to and broken down within the liquid. There is consequently no definite molecular weight to be ascribed to water or ammonia, in the liquid state.

286. Predicting Solubility

A chemist can usually guess rather accurately whether a given substance will dissolve in a given solvent:

1. *Ionic crystals* (including alkalies and many or most salts, § 142) are usually so strongly knit together by the mutual attraction of oppositely charged ions that they can be brought into solution only by *highly reactive* (*highly polar*) solvents, such as water or ammonia. These combine with the ions in the process of dissolving the crystal (§§ 250, 364).

2. *Molecular crystals* are relatively weak, hence are readily torn down and dissolved by a great variety of *non-polar* or *moderately polar* solvents. Examples are iodine, dissolving in carbon tetrachloride or chloroform, and sulfur, dissolving in carbon disulfide.

3. *Molecular crystals* commonly do not dissolve in the most polar solvents unless they possess reactive groups of atoms, which by reaction with the solvent may furnish the energy needed for overcoming the attraction of the polar solvent molecules for one another.

4. *Maximum solubility* is obtained when minimum energy is expended in transferring molecules of one substance into the interior of another. This happens whenever solvent and solute molecules are closely related, chemically.

Thus we account for the fact that "like dissolves like." We may dissolve petroleum and other hydrocarbons in gasoline or benzene, which are themselves hydrocarbons. We may dissolve one alcohol in any other alcohol of not too dissimilar molecular structure. Fats of all sorts intermingle freely with one another in lard substitutes; waxes intermingle freely in furniture or automobile polish.

287. Some Applications

Let us see how the rules just given work out in a few cases:

1. *Difficultly condensable gases* (H_2, O_2, N_2, He, etc.) are so because their molecules are nearly non-polar, hence attract one another only

very slightly. For the same reason their molecules are but slightly attracted by solvent molecules. The difficultly condensable gases are therefore but slightly soluble in all solvents.

2. *More readily condensable gases* are so because their molecules are somewhat polar, and consequently attract one another more strongly. For the same reason they are more strongly attracted by solvent molecules, particularly by those that are conspicuously polar.

3. *A few readily condensable gases* (HCl, HBr, HI, NH_3) are so constituted as to *react* readily and completely with water, the water either accepting protons (hence acting as a *base*) or losing protons (hence acting as an *acid*). Such gases are therefore readily soluble in water.

4. *Molecular crystals* (iodine, camphor, naphthalene, etc.) ordinarily fail to dissolve in water, since the forces acting between the molecules of this highly *polar solvent* are so strong that it is difficult for any foreign molecule to penetrate between them. Molecular crystals that contain highly reactive or highly polar groups of atoms (OH groups, for example, in glycerol or cane sugar) are likely to be soluble in water. We have even met oily acids (§§ 131, 132) that spread over water to form surface films one molecule deep, because one end of each molecule is soluble in water, and the other end insoluble. (Ex. 1–3.)

288. Solubility of Ionic Crystals

The smaller the charges carried by the ions of a crystal and the larger the ionic radii the weaker the forces that bind the ions to one another within the crystal, and the more readily the crystal structure is broken down. Thus we account for the ready solubility in water of potassium nitrate (K^+, NO_3^-) in which we have univalent ions, as compared with the slight solubility of calcium carbonate (Ca^{++}, CO_3^{--}), in which we have divalent ions (Ca^{++}, moreover, being smaller than K^+).

In the following table, observe that *the only classes of salts invariably soluble in water are those composed of univalent ions of rather large radius.* On the contrary, there are very few soluble salts in which both ions are divalent or tervalent. Completely to account for differences in solubility, we should doubtless also have to consider the tendency of the ions toward being hydrated, and the geometric structure of crystals (since certain structures are inherently more stable than others). (Ex. 4–7.)

Soluble in Water

1. All sodium, potassium, and ammonium salts (a few are only slightly soluble).
2. All nitrates, acetates, chlorates, and perchlorates (except a few hydroxy-salts, § 399).

Relatively Insoluble in Water

1. Chlorides, bromides, and iodides of Ag^+, Hg_2^{++}, Pb^{++}. Observe that this is mercury in its lower valence (mercur*ous* salts). The corresponding mercur*ic* salts (Hg^{++}) are soluble.
2. Sulfates and chromates of Ag^+, Hg_2^{++}, Pb^{++}, Ca^{++}, Sr^{++}, Ba^{++}. This, again, is mercur*ous* mercury.
3. Sulfides of all metals except the alkali metals (Li^+, Na^+, K^+, NH_4^+, etc.) and the alkaline-earth metals (Be^{++}, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}). The light metal (soluble) sulfides are *ionic* sulfides. They are completely hydrolyzed by water. The heavy metal (insoluble) sulfides are non-ionic.
4. Oxides, hydroxides, carbonates, oxalates, borates, fluorides, phosphates, and silicates of all metals except the alkali metals and NH_4^+. The phosphate and carbonate of lithium differ from the corresponding salts of the other alkali metals in being very slightly soluble.

289. Unsaturated, Saturated, and Supersaturated Solutions

When a lump of sugar is dissolved in a cup of tea we have a solution that is still *unsaturated*, for it will dissolve a second lump, then further lumps. At last a saturated solution is obtained, in which no more sugar can be made to dissolve, except by increasing the temperature. Nevertheless, if we do increase the temperature in any such instance, more of the solid will ordinarily dissolve. If we then filter the solution, and bring it back to the former temperature, it will often retain all the extra material that it previously dissolved, hence will be *supersaturated*.

One cannot tell whether a solution is unsaturated, saturated, or supersaturated, from its appearance or from any of its properties, except by one test: Drop into it a crystal of the solute in solid form, even a microscopic crystal. According as the crystal dissolves, remains unaltered in size, or induces crystallization, we conclude that the solution is unsaturated, saturated, or supersaturated.

A supersaturated solution, when protected from dust and evaporation, will often retain its surplus dissolved material indefinitely. But the minutest trace of that material in solid form may cause so many crystals to separate that the flask may sometimes be inverted without any liquid spilling out. The need for a crystal fragment to induce crystallization in a supersaturated solution is precisely that already given (§ 157) for inducing a supercooled pure liquid to freeze by the same expedient.

290. Solutions of Gases in Liquids. Law of Henry

We have learned (§ 122) that a liquid is a liquid because its molecules have sufficient attraction for one another to be restrained within a definite total volume. In the absence of such attractive forces its molecules would scatter indefinitely, and the liquid would become a gas or vapor.

So, when a gas is placed in contact with a liquid, the molecules of the gas find little free space into which they can penetrate, between the molecules of liquid. The total solubility of a *non-polar* gas (H_2, O_2, N_2, H_2, A, CH_4, etc.) in any liquid is therefore very small (only 2 to 5 volumes in every 100 volumes of liquid, at room temperature).

The molecules of a non-polar, hence slightly soluble, gas, which have penetrated between the molecules of a liquid, are not appreciably attracted by the latter. So the *density* of the dissolved gas (the weight dissolved in unit volume) is proportional to the pressure upon it, just as if the gas were undissolved. In other words, *when a gas is only slightly soluble the weight dissolved in any given quantity of solvent is proportional to the pressure upon it.* This is *Henry's Law,* first stated by Joseph Henry, a distinguished American physicist of a century ago. (Ex. 8–10.)

But when a gas in contact with a liquid is distinctly *polar* (CO_2, SO_2, H_2S, etc.) strong attractive forces exist between its molecules and the molecules of the liquid. So its molecules are dragged into the liquid, even prying the liquid molecules apart. A dissolving polar gas may *react* with the liquid to some extent, often forming addition compounds (H_2CO_3, H_2SO_3, etc.). Its solubility may then amount to several hundred volumes in 100 volumes of liquid, at room temperature. If the dissolving gas is extremely reactive (HCl, NH_3, etc., dissolving in water) several thousand volumes may dissolve in 100 of liquid, at room temperature. Increasing the pressure on a polar or reactive gas somewhat increases the weight of gas dissolved, but not nearly so much as would be indicated by Henry's Law, which we have emphasized applies only to slightly soluble gases.

When a gas has been dissolved under pressure, the release of pressure leaves the gas molecules trapped within the interior of the liquid. The liquid is then *supersaturated* with gas. Next time you lift the cap of a bottle of pop do it cautiously. You will have a supersaturated solution of carbon dioxide in sweetened and flavored water. Shake it, and it will foam violently as the gas escapes, leaving a solution that is merely *saturated*, at the given temperature and pressure.

The weight of gas which a liquid can dissolve falls off very rapidly with increased temperature. The decrease is much greater than can be accounted for by the decreased density that any gas has at higher temperatures. The molecules of liquid evidently move more and more energetically as the temperature is increased, and expel some of the gas molecules which at lower temperatures had penetrated between them.

When a liquid is boiled the escaping vapors soon carry away the last traces of any gas which has not actually entered into a reaction with the solvent. Thus water, by being boiled, may very quickly be freed from dissolved air, and more slowly from dissolved carbon dioxide.

291. Saturation as an Example of Equilibrium

It is easy to see why a solid, dissolving in a liquid, ordinarily will not dissolve indefinitely. A situation is finally reached in which molecules are removed from the surface of the solid and dispersed through the liquid exactly as fast as other molecules of the same kind return from the interior of the liquid and become reattached to the solid. The solid is then said to be in *equilibrium* with the solution, and the solution is definitely saturated.

Solution and redeposition do not cease after equilibrium is attained. They merely continue indefinitely to balance. This can be proved by a simple experiment: Hang a broken or irregular crystal in a saturated solution of that substance. It will neither increase nor decrease in weight. Nevertheless, it will improve its form, by the dissolving of material from certain faces and edges and redeposition elsewhere.

292. Rate of Solution and Weight Dissolved

A material will dissolve most rapidly when it is finely ground. As more and more dissolves, the rate of solution gradually slows down, approaching zero as the solution approaches complete saturation. We commonly stir a liquid while dissolving anything in it, else the liquid in contact with the dissolving material would be nearly saturated from the beginning, and the rate of solution would be greatly lessened. Even with the most vigorous stirring the dissolving material is always coated with *a thin film of saturated liquid*, through which solvent molecules approach the dissolving solid, and through which dissolved material is removed only very slowly, by *diffusion. This surface film is the factor that chiefly limits the rate of solution, in most cases.*

Increased temperature increases (1) the frequency with which solvent molecules collide with the surface of the dissolving material, and

also (2) the rate at which material just dissolved is carried away through the surface film by diffusion.

With most solids, increased temperature not only speeds up the process of solution, but also increases the total weight dissolved (Fig. 105). A few solids (calcium sulfate, for example) decrease in solubility in water as the temperature is increased. (Ex. 11–13.)

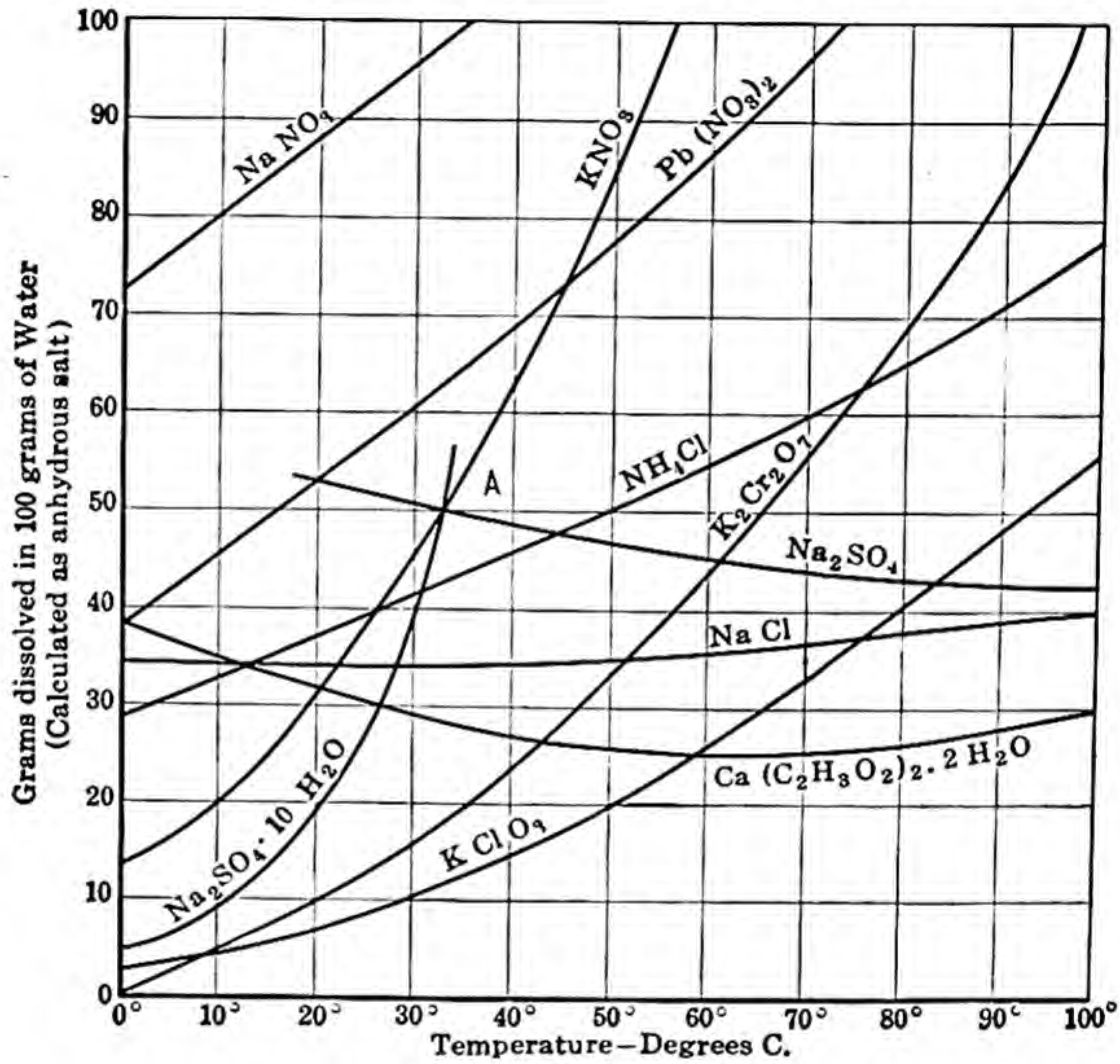


FIG. 105. Solubility curves.

293. Different Ways for Expressing the Composition of a Solution

The composition of a solution may be expressed in several different ways:

1. **Percentage of solute, by weight.** This gives the number of grams of *solute* in 100 grams of *solution.* A 10 per cent solution, for example, contains 10 grams of solute for every 90 grams of solvent, making a total of 100 grams.

Sometimes information about the *percentage strength* of a solution, by weight, needs to be used in connection with a statement about the *density* of the solution (usually in grams per milliliter). Obviously (Appendix H),

$$\text{ml} \times \frac{\text{g}}{\text{ml}} = \text{g}$$

So 100 ml of a solution having a density of 1.15 g/l has a total weight of 115 grams. (Ex. 14.)

2. **Mole-fraction** of each component (§ 118). Remember that the sum of the mole-fractions of all the components of a solution is always 1.0 (*i.e.*, is the whole solution). (Ex. 15.)

3. **Molality,** *i.e.*, the number of *moles* or *gram-formula weights* (§ 115) of solute, dissolved in 1000 grams of *solvent*. A *molal* solution is one containing 1 mole (or 1 gram-formula weight) in 1000 grams of solvent. (Ex. 16, 17.)

4. **Concentration.** This gives the *weight of solute*—expressed in grams, moles, formula weights, or equivalents (defined below)—*in 1 liter of solution*. In other words, concentration relates to a definite total *volume* (1 liter) instead of to a definite total *weight* or *number of moles*.

Because the volume of every solution varies somewhat with varying temperature, its concentration does, too. Its weight percentage or its composition (expressed as a mole-fraction or molality) of course do not.

294. Equivalents. Normal Solutions

We have just said that the concentration of a solution is sometimes expressed in *equivalents* of solute, in 1 liter of solution. An *equivalent* of any substance is the fraction of a gram-formula weight that corresponds to *one unit of positive or negative ionic valence* (for an acid, base, or salt) or to *unit change in valence or valence number* (for an oxidant or reductant). A *milliequivalent* is as many milligrams as there are grams in an equivalent. It is therefore 1/1000 of an equivalent.

In potassium nitrate, KNO_3, for example, the ions are K^+ and NO_3^-. Thus a gram-formula weight (*i.e.*, KNO_3 = 101 grams) corresponds to unit positive or negative valence, and thus is one equivalent; but in sodium phosphate, Na_3PO_4, the ions are $3Na^+$ and PO_4^{---}. A gram-formula weight (*i.e.*, Na_3PO_4 = 164 grams) therefore corresponds to three units of positive or three units of negative valence, and is thus three equivalents. One equivalent would be one third of the gram-formula weight, or $\frac{1}{3} \times 164 = 54.7$ grams (Ex. 18, 19.)

A solution that contains one equivalent of dissolved material in a liter of solution (or one milliequivalent in 1 ml of solution) is called a *normal solution* (usually abbreviated N). Solutions of twice this concentration are said to be double-normal (usually written $2N$). Other solutions may be half-normal ($0.5N$ or $N/2$) or one-fifth normal $0.2N$ or $N/5$). (Ex. 20.)

Solutions of known *normality* (namely, those containing a known number of equivalents per liter of solution) have a great practical advantage: *A solution of a given normality will react with its own volume of any other solution of the same normality.* For example, 20 ml of any N acid will react with 20 ml of any N alkali, 40 ml of any $N/2$ alkali, or 100 ml of any $N/5$ alkali. Thus we practically eliminate calculations to determine what relative volumes of reagents should be used in laboratory work. All that is needed is a preliminary calculation, to establish the normality, when each solution is first prepared. Normal solutions play such an important part in practical chemical work that the student should pause now to work a sufficient number of problems to master the idea.

$$\text{ml} \times \text{normality} = \text{milliequivalents (meq.)}$$

$$\text{liters} \times \text{normality} = \text{equivalents (equiv.)}$$

(Ex. 21–29.)

295. The Vapor Pressures of Solvent and Solute

The vapor pressure of solvent evaporating from a solution is always less than the vapor pressure of the pure solvent at the same temperature. We need not be surprised. The solvent has a *lower concentration* in the solution than it has in the pure solvent. Moreover, for one substance to dissolve in another their molecules must attract each other strongly. This attraction not only retains the dissolved substance in solution but also reduces the tendency of the molecules of solvent to escape into the vapor.

The vapor pressure of the solvent in a dilute solution is proportional to its mole-fraction (§ 118) (*Raoult's Law*). For example, in a solution containing one mole (342 grams) of cane sugar, $C_{12}H_{22}O_{11}$, dissolved in 99 moles (1782 grams) of water, thus making a total of 100 moles, the mole-fraction of the solvent is 0.99. The vapor pressure of the water evaporating from the solution is thus about 99 per cent of the vapor pressure of pure water at that temperature. In a *concentrated solution*, even one so moderately concentrated as in the example just considered, each component so modifies the properties of the other that Raoult's Law does not hold very exactly.

When volatile liquids dissolve completely in each other, each lowers the vapor pressure of the other. In what is termed an *ideal solution* the components are miscible in all proportions and the vapor pressure of each component, at all concentrations, is strictly proportional to its mole-fraction, as shown in Fig. 106.

Solutions in which the components are chemically similar (benzene and toluene, for example) behave most nearly as just described, *i.e.*, are most nearly ideal. (Ex. 30–33.)

A mixture that departs very widely from ideal behavior is shown in Fig. 107. Observe that the vapor pressure of either component most closely approaches the ideal pressure (shown by the dotted line) when the mole-fraction of that component approaches 1.0, in other words, when that component serves as a *solvent*, to dissolve *a small amount of the other material.*

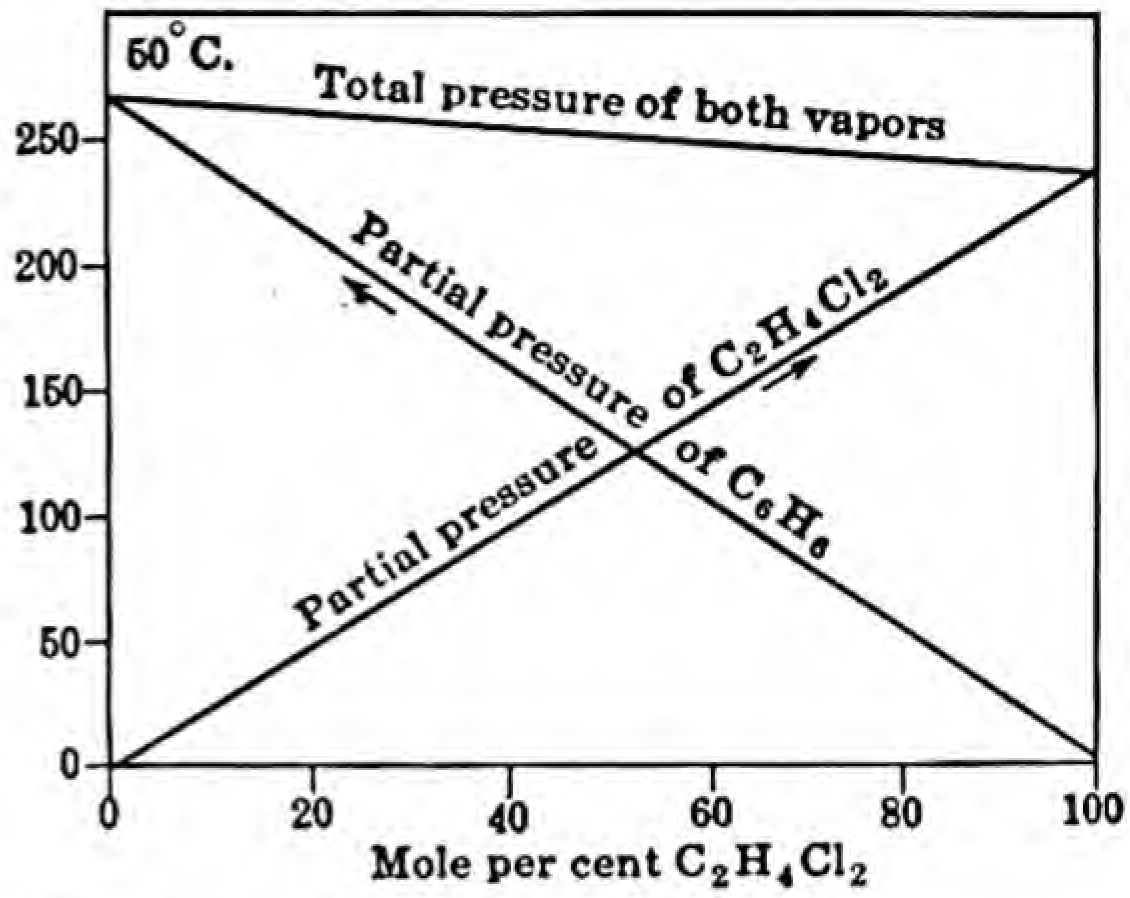


FIG. 106. Partial vapor pressures in an ideal solution (ethylene dichloride and benzene).

When a substance is practically non-volatile its vapor pressure is practically zero. Then all the vapor pressure of a solution of the substance must be due to the *solvent.* By comparing this vapor pressure with that of the *pure solvent* it is easy to determine the molecular weight of the dissolved non-volatile substance.

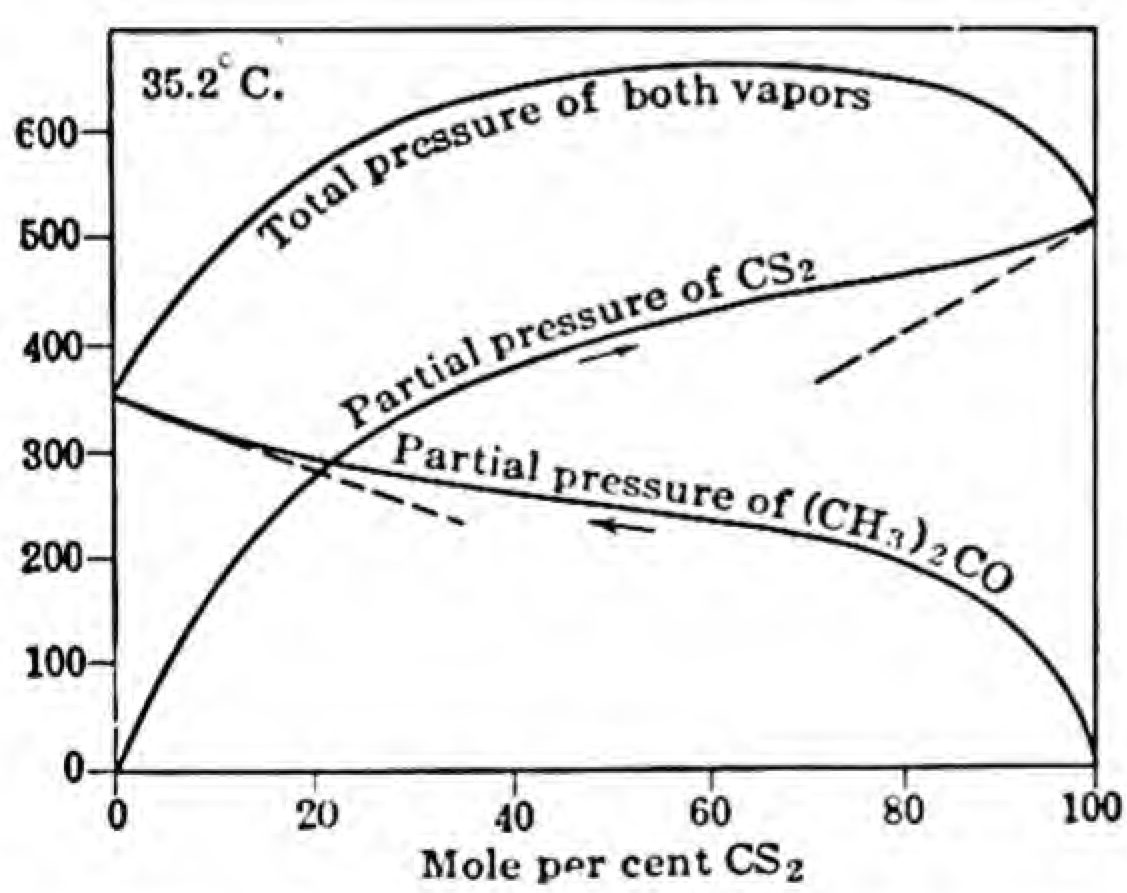


FIG. 107. Partial vapor pressures in a non-ideal solution (carbon disulfide and acetone), showing a maximum total vapor pressure, hence a minimum boiling point, at about 70 mole per cent carbon disulfide.

For example, let us assume that the vapor pressure of a non-volatile substance in a volatile solvent has been found to be 0.98 of the vapor pressure of the pure solvent. Then the mole-fraction of the solvent (by Raoult's Law) must be 0.98 and that of the solute must be $1 - 0.98 = 0.02$. If the solution actually contains 5 grams of dissolved solute for each mole of solvent (nearly enough, for each mole of total) then the 5 grams must represent 0.02 mole. A full mole would then be 250 grams, and the molecular weight of the dissolved substance would be 250. (Ex. 34–37.)

Molecular weights are seldom determined by this method, since precise vapor pressure measurements are experimentally difficult.

296. Boiling Point and Freezing Point of a Solution

In Fig. 108 we have sketched the vapor-pressure curve of pure water and of a solution.

Since the solvent in a *solution* has a lower vapor pressure than the *pure solvent* does, we must reach a higher temperature before its vapor pressure will equal any specified pressure. In other words, *dissolving a non-volatile*[2] *solute in a solvent will raise the boiling point.* In our sketch the increase of the boiling temperature is represented by ΔT_b.

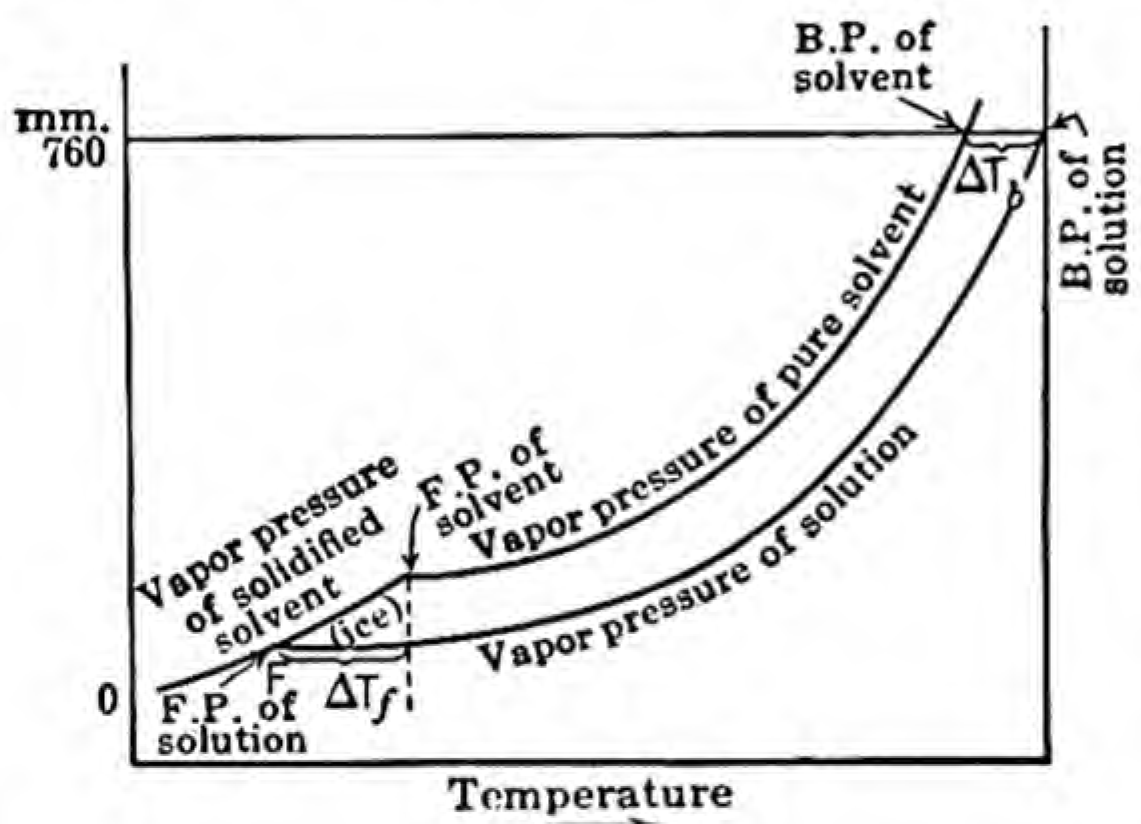


FIG. 108. Effect of a dissolved non-volatile solute in decreasing the vapor pressure, raising the boiling point, and lowering the freezing point.

In freezing a solution we must cool the solution down to some temperature below the freezing point of the pure solvent, until the vapor-pressure curve for the solution intersects that for ice (the point F, in our diagram). Solution, vapor, and ice may coexist indefinitely at that temperature. In our sketch the lowering of the freezing point is represented by ΔT_f.

297. Molecular Weights from Freezing Points and Boiling Points

For a dilute solution, the elevation of the boiling point or lowering of the freezing point (in comparison with the boiling or freezing point of the pure solvent) *is proportional to the molality* (that is, to the number of moles of solute dissolved in 1000 grams of solvent). It does not depend on the nature of the solute.

The freezing point of water, for example, *is lowered at the rate of 1.86°C for each mole of solute in* 1000 *grams of water, provided that the solution is not very concentrated.* If $\frac{1}{100}$ mole (3.42 grams) of cane sugar, $C_{12}H_{22}O_{11}$, is dissolved in 1000 grams of water, the freezing point of this solution should therefore be $0.01 \times 1.86 = 0.0186$°C below the freezing point of water. Conversely, from the lowering of the freezing point or elevation of the boiling point produced by a

[2] A *volatile* solute will lend its own vapor pressure to assist that of the solvent in driving back the atmosphere, hence the boiling point may sometimes be *lowered.*

given weight of solute in 1000 grams of solvent, we may conclude how many moles of the solute are in the weight taken, and accordingly what the molecular weight must be. (Ex. 38–40.)

Ionic substances, in extremely dilute solutions, behave as if each ion were an independent molecule and hence yield molecular weights, in measurements of freezing points or boiling points, that are very nearly an average of the ionic weights. For example, KCl (corresponding to the *two* ions, K^+ and Cl^-) lowers the freezing point at very nearly the rate of $2 \times 1.86°$ for each gram-formula weight dissolved in 1000 grams of water; K_2SO_4 (corresponding to the *three* ions $2K^+$ and SO_4^{--}) lowers the freezing point at the rate of $3 \times 1.86°$; $K_3Fe(CN)_6$ (corresponding to the *four* ions $3K^+$ and $Fe(CN)_6^{---}$) lowers the freezing point at the rate of $4 \times 1.86°$. Here is one of the strongest arguments in favor of the idea that these and most other salts, in solution in water, exist as separate, nearly independent *ions.*

For more concentrated solutions observations are complicated by hydration of the ions and especially by interionic attraction (§ 419), which prevents the ions from having the complete independence of action which we assumed for uncharged particles or for ions in extremely dilute solutions. (Ex. 41.)

298. Fractional Distillation

Volatile liquids may be freed from non-volatile impurities by *distillation.* Even a mixture of two or more volatile liquids may be partially or completely separated by *fractional distillation.* In its simplest form this is merely ordinary distillation, with the *distillate* collected in a number of successive portions called "fractions." *The first fraction will contain the highest proportion of the most volatile component of the mixture.* Subsequent fractions will contain increasing proportions of the less volatile components.

These successive fractions usually need to be separately *redistilled,* the least volatile portion of each being combined with the next fraction before redistilling the latter. If the ingredients of the liquid mixture have reasonably different boiling points, repeated redistillation will often separate them almost completely. The process of repeated fractional distillation may be very much shortened, and complete separation is sometimes obtained in a single operation, if the vapors, on the way from still to condenser, are made to pass through a *fractionating column* or *distilling column,* Fig. 109 (next page), containing a series of screens or plates, on each of which some condensation and reevaporation occur, as if in a miniature still.

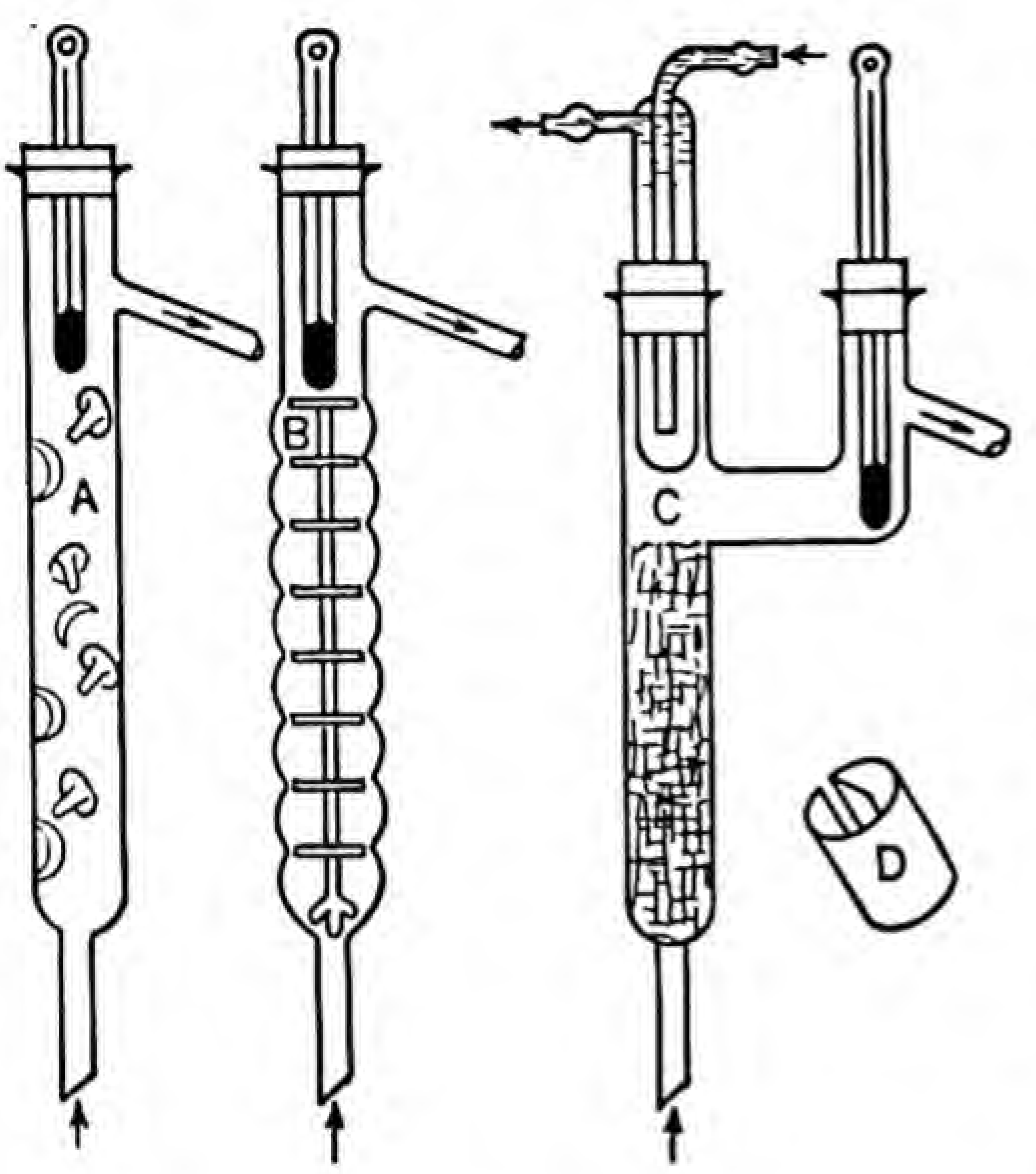


FIG. 109. Distilling columns. In the form shown at *A*, the ascending vapor partially condenses on the walls of the column, forming a liquid that trickles off the little points, flows over the oppositely placed welts, and there yields up its more volatile components to the ascending vapor, as if redistilled.

In the form *B*, a little liquid, condensed on each of the flat plates, yields up its more volatile components to the ascending vapor. In the form *C*, a small condenser at the top of the column recondenses perhaps 80 per cent of the material. This runs down through a long column, filled with bent pieces of metal, of the shape shown at *D*. Reevaporation of the more volatile components takes place at the surface of these pieces.

299. Steam Distillation

A liquid whose boiling point is very high may sometimes be vaporized at a much lower temperature by passing a current of steam through it—often *superheated steam*, namely, steam that has been passed through a hot tube to raise it to a temperature above that at which

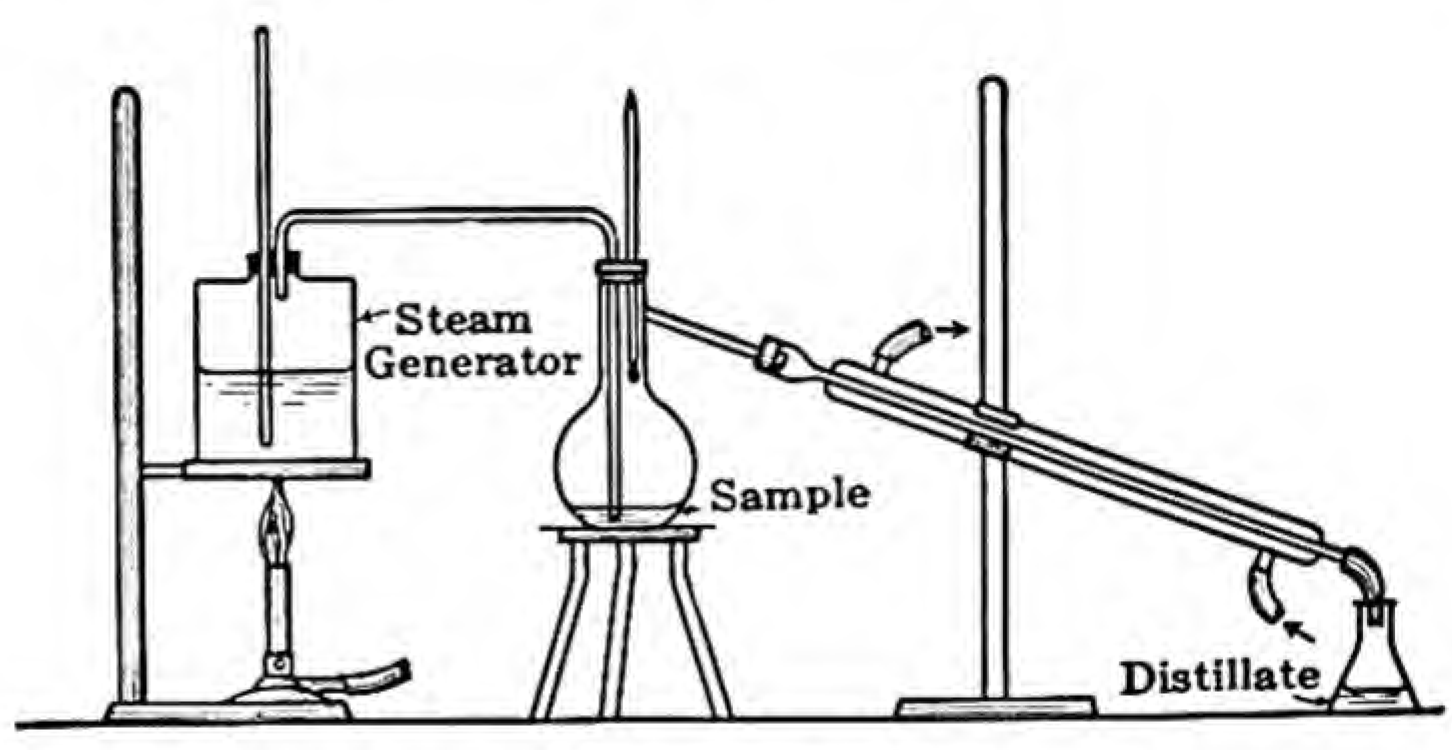


FIG. 110. Steam distillation.

it originally vaporized. The superheated steam helps overcome the pressure of the atmosphere and favors evaporation by carrying away the vapors that escape from the high-boiling liquid.

The steam and the vapors of the other substance, passing together into the condenser, separate into two distinct liquid layers, if the other substance is but slightly soluble in water (Fig. 110). This

process is commonly used in vaporizing tar, aniline, and other substances that are not decomposed by steam and are but slightly soluble in water. The superheated vapors of any other liquid may, of course, be substituted for superheated steam.

When the substance being distilled with steam is insoluble in water, this substance and water pass into the distillate in a ratio of moles that is the same as the ratio of vapor pressures of the two substances at the distillation temperature. Thus, if the substance being distilled has a vapor pressure of 67 mm and steam of 670 mm (barometric pressure, 737 mm), then 1 mole of the substance will pass into the distillate for every 10 moles of water. This is a consequence of Dalton's Law of Partial Pressures (§ 118). (Ex. 42–44.)

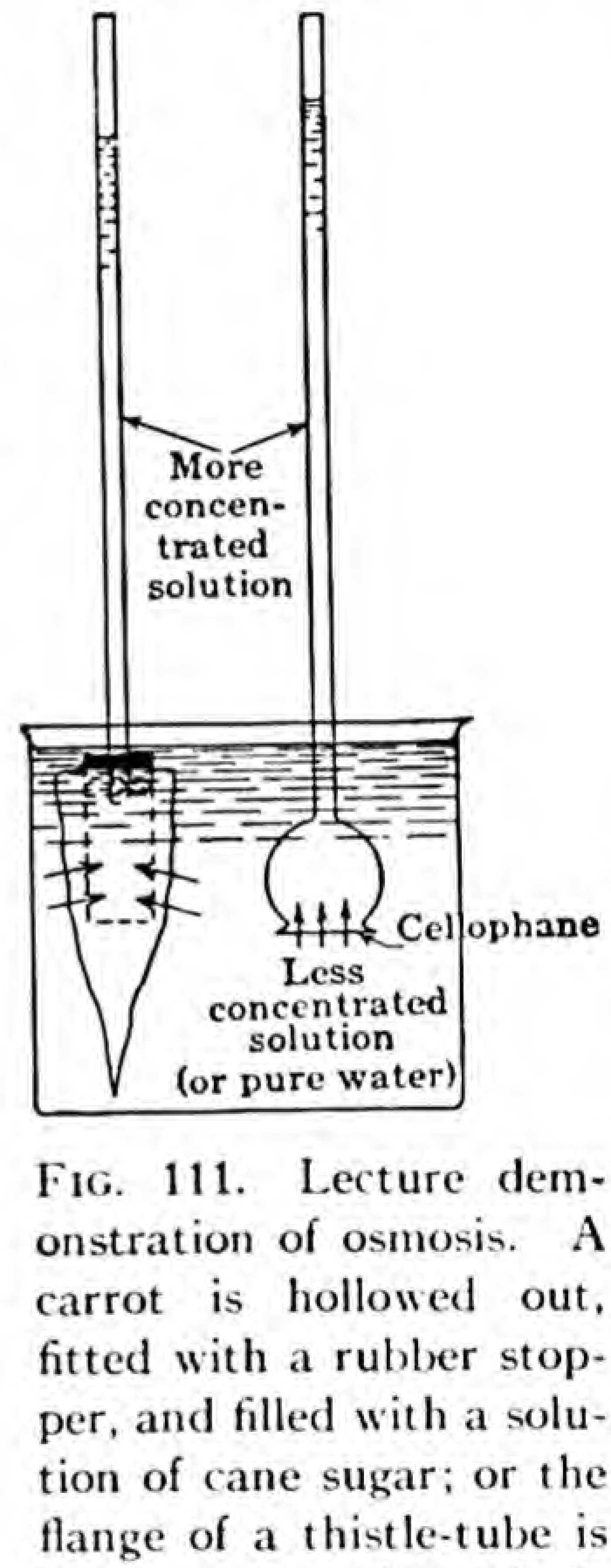


FIG. 111. Lecture demonstration of osmosis. A carrot is hollowed out, fitted with a rubber stopper, and filled with a solution of cane sugar; or the flange of a thistle-tube is covered with a sheet of cellophane, the edge being made water-tight by being painted with collodion. (Impermeable cellophane may be rendered water-permeable by being soaked in acetone.)

300. Osmosis

If a membrane into which a solvent readily penetrates is used to separate two solutions of different concentrations (Fig. 111), we invariably find that *some of the solvent passes through the membrane from the less concentrated into the more concentrated solution.* The level of the more concentrated solution will therefore slowly rise.

The incoming solvent, penetrating through a membrane from a pure solvent into a solution, sets up a pressure called the *osmotic pressure.* We can measure this by noting what pressure needs to be applied to the solution to stop the entrance of solvent through the membrane. The osmotic pressure may amount to many atmospheres, in solutions of moderate concentration.

A membrane through which a solvent penetrates, while the solute is held back, is called a *semi-permeable membrane.* The flow of the solvent through a membrane, from a less concentrated into a more concentrated solution, is called *osmosis* (or, occasionally, *osmotic flow*).

Osmosis need not seem mysterious. A dissolved solute decreases the tendency of a solvent to escape from a solution into a membrane for

the same reasons that it reduces the tendency of the solvent to escape into a vapor (§ 295). So, if we have a membrane wet by solutions of two different concentrations, molecules from the *low-concentration* solution penetrate that side of the membrane *more* frequently, and return from the membrane *less* frequently, than they do on the high-concentration side. The result is a continuous flow of solvent through the membrane.

For dilute solutions, osmotic pressure has been found to be proportional to the *concentration* of solute molecules and to the *absolute temperature*. Indeed, the same equation, $PV = nRT$, holds for very dilute solutions as for an ideal gas (§ 119), except that P in this instance is the osmotic pressure, and n is the number of moles or gram ions of *solute* dissolved in the total volume, V. (Ex. 45.)

Osmosis and osmotic pressures have occasioned endless discussion and experiment on the part of biologists, since living membranes are semi-permeable and act as osmotic membranes. The passage of mineral salts from the soil into the rootlets of plants, the ascent of sap in trees, the swelling of seeds when germinating, and the transfer of nutrient materials from the blood stream into animal cells and tissues are all examples of complicated phenomena in which osmosis plays a part. For interesting details the reader is referred to textbooks of plant or animal physiology. (Ex. 46.)

Technical Words

Dispersion, p. 332. **Colloidal dispersion,** p. 332. **Solution,** p. 332.
Solvent, p. 333. **Aqueous solution,** p. 333.
Soluble (a word often misspelled)—capable of being dissolved.
Solute, p. 333. **Complete miscibility,** p. 333.
Polar or dipole molecule, p. 333. **Polar substance,** p. 333.

Dipole moment—a measure of the tendency of a dipole to become oriented in an electric field. If positive and negative charges were concentrated at two points a definite distance apart, then either charge, multiplied by the distance between them, would give the dipole moment.

Dielectric constant—a measure of the ability of a material to weaken the force that an electrically charged body exerts upon another, when the given material intervenes. High dielectric constant indicates that the given material has great ability to weaken the electric forces and has highly polar molecules. The strongest electrical force between two charged bodies would be that exerted across a vacuum (dielectric constant unity).

Concentrated—containing a relatively large amount of dissolved material in any given volume of solution.

Dilute—containing a relatively small amount of dissolved material in any given volume of solution.

Saturated (with reference to a *solution*)—containing as much dissolved material as can be retained in solution at the given temperature, in the presence of undissolved material of the same sort.

Unsaturated, supersaturated (with reference to a solution)—having a concentration that is respectively less or greater than that of a saturated solution at the given temperature. Test to determine whether a solution is unsaturated, saturated, or supersaturated, p. 337.

Mole, p. 124. **Gram-formula weight,** p. 124. **Percentage by weight,** p. 340.
Molal solution, p. 341. **Molality,** p. 341. **Concentration,** p. 341.
Equivalent, p. 341. **Milliequivalent,** p. 341. **Normal solution,** p. 341.
Normality, p. 342. **Molar concentration**—moles solute per liter of solution.

Solvation—the chemical union of solvent molecules with molecules or ions of a dissolved material.

Hydration—*solvation* in the special case in which water is the solvent.

Escaping tendency—the tendency of solvent molecules to escape from a solution (by evaporation, freezing, penetration of a membrane, etc.). It is proportional to the *effective concentration* (activity) of the solvent in the given solution.

Ideal solution—a solution in which each component possesses an *escaping tendency* and hence a *vapor pressure* that is proportional to its mole-fraction, independently of the nature or amount of any other component.

Distillate—material that has been distilled.

Fractional distillation, p. 346. **Fractionating or distilling column,** p. 346.
Superheated steam, p. 346. **Semi-permeable membrane,** p. 347.
Osmosis, p. 347. **Osmotic pressure,** p. 347.

Isotonic solutions—solutions that set up the same osmotic pressure when they are separated by a semi-permeable membrane from a pure solvent (usually water), and which consequently do not display osmotic flow when they are separated *from each other* by a semi-permeable membrane. If living cells (*e.g.*, blood corpuscles) are placed in solutions that are isotonic with the cell contents, the cells neither swell nor shrink.

Plasmolysis—the shrinkage of cell protoplasm due to the passage of water outward through the cell walls by osmosis, when the material is placed in a solution of greater than isotonic concentration.

Exercises

1. From the general rules in § 287 predict whether camphor, which forms molecular crystals, is soluble or insoluble in chloroform and in water.

2. Suggest some probable solvents for a hydrocarbon (non-polar). Will it probably dissolve in water?

3. Explain why substances of complicated structure and high molecular weight are frequently difficult to dissolve in any solvent.

4. Write an ionic equation for the precipitation of one substance in each of the four insoluble groups of substances in § 288.

5. If the ions of a crystal have a strong tendency to become hydrated does this tend to make the crystal soluble or insoluble in water?

6. Silver fluoride, in contrast with the remaining silver halides, is readily soluble in water. Which ion is responsible?

7. Would you expect the arsenates of most heavy metals to be soluble or insoluble? Why?

8. If 1 millimole of nitrogen dissolves in a certain volume of water, under a pressure of 1 atm, what actual weight, in milligrams, will dissolve under a pressure of 380 mm? 140

9. About 2 moles of oxygen dissolve in water for every mole of nitrogen when the two gases are under equal pressures. About how many moles of oxygen will dissolve for each mole of nitrogen, when the nitrogen is present under a partial pressure of 0.8 atm, and the oxygen under a partial pressure of 0.2 atm (as they are, very nearly, in ordinary air)? 500

10. How many moles of carbon dioxide will be needed to saturate a liquid under 5 atm pressure, if 22 grams are needed under 1 atm pressure? 250

11. From Fig. 105, p. 340, determine what weight of $K_2Cr_2O_7$ will separate if 100 grams of water, saturated with that salt at 90°C, is allowed to cool to 20°C. 740

12. What weight of water (Fig. 105) is needed to dissolve a gram-formula weight (§ 115) of $KClO_3$ at 80°C? 300

13. How many moles of water (Fig. 105) are needed to dissolve a gram-formula weight of NH_4Cl at 80°C? 450

14. What weight of solute is contained in 1 liter of a solution of density 1.05 g/ml, if it is a 5 per cent solute? 525

15. What is the mole-fraction of each component in a solution containing 288 grams of water and the same weight of methyl alcohol, CH_3OH? 640, 360

16. What weight of cupric sulfate pentahydrate (§ 145) must be dissolved in 500 grams of water to make a molal solution? 125

17. A solution has a density of 1.25 g/ml. What is the weight of 1 liter of this solution? If this is a 20 per cent solution, containing a solute of molecular weight 100, what is the molality (§ 293) of the solution? 125, 250

18. What fraction of a mole makes an equivalent of each of the following: $ZnCl_2$, K_2SO_4, CaS, $Mg(ClO_3)_2$, NH_4Br, Ag_2CrO_4, $NaHSO_3$, H_3PO_4, HF, $Ca(OH)_2$?

One mole is how many *milliequivalents* of each of these substances?

19. What is the valence number (§ 171) of manganese in MnO_2 and in $MnCl_2$, respectively? What change in valence number takes place? Then what fraction of a formula weight of MnO_2 makes an equivalent, when MnO_2 serves as an oxidizing agent, being reduced to $MnCl_2$? 500

20. What weight of common salt is contained in a liter of $0.125N$ (namely, $N/8$) solution? 731

21. What volume of any $N/5$ alkali is needed to react with 25 ml of any $N/2$ acid?

22. How many milliequivalents in 20 ml of $N/5$ solution? 400

23. How many milliequivalents of any other substance are needed to react with 20 ml of $N/5$ solution? 400

24. If 20 ml of $N/5$ acid react with 20 ml of $N/4$ alkali, which reagent is in excess, and how many milliequivalents of it? 100

25. What weight of anhydrous sodium carbonate would you dissolve to prepare 5 liters of $N/4$ solution? 663

26. How many milligrams of potassium sulfate in 5 milliequivalents? In 25 ml of $N/5$ solution? 435

27. In 980 mg of hydrogen sulfate (H_2SO_4) how many millimoles and how many milliequivalents are there? What volume of $N/5$ solution will it make?

100, 200, 100

28. What weight of NaOH is neutralized by 25 ml of an acid which is 1.20*N*? 120

29. A saturated solution of $Pb(NO_3)_2$ at 70°C (Fig. 105) is how many times molal? 293

30. Two volatile liquids have molecular weights of 100 and 200, respectively. What is the mole-fraction of each in a mixture containing equal weights of each? 667, 333

31. The first of the two liquids just mentioned exerts a vapor pressure of 90 mm and the second of 45 mm, at a certain temperature. Use the results of the preceding exercise to determine the total vapor pressure of a mixture of equal weights of the two liquids, if they form an ideal solution. 750

32. What weight of carbon disulfide must be mixed with 90 grams of carbon oxysulfide, COS, to give an ideal solution having a vapor pressure midway between those of the two pure liquids? 114

33. Water and glycerol are miscible in all proportions, but glycerol is practically non-volatile. What weight of glycerol must be mixed with 100 grams of water to obtain a solution with a vapor pressure one-fifth that of water at the same temperature? Glycerol is $C_3H_5(OH)_3$. 203

34. An aqueous solution of a non-volatile substance has a vapor pressure of 49.75 mm, at a temperature at which water itself has a vapor pressure of 50 mm. What is the mole-fraction of water and of the solute? How many moles of the solute in 100 moles of solution (nearly enough, in 100 moles of *water*)? 995, 500

35. The solution in the preceding exercise was prepared by dissolving 40 grams of the given substance in 100 moles of water. Compare with the result of the preceding exercise to determine the molecular weight of the substance. 800

36. When a specified weight of a non-volatile substance is dissolved in benzene the vapor pressure is lowered from 200 mm to 195 mm. What is the mole-fraction of benzene and of the solute? 975, 250

37. How many moles of the substance in the preceding exercise are present for every 100 moles of solution (nearly enough for every 100 moles of *benzene*)? If the substance has a molecular weight of 100, how many grams of it were present for every 780 grams of benzene (C_6H_6)? 250

38. What is the freezing point of a solution obtained by dissolving 0.5 gram of a substance of molecular weight 50 in 1000 grams of water? 186

39. If the freezing point of a solution is observed to be 0.186° below the freezing point of water, what fraction of a mole of the solute is dissolved in each 1000 grams of water? Actually, 0.5 gram of this solute is dissolved in 20 grams of water. What is its molecular weight? 100, 250

40. What weight of a substance of molecular weight 200 must be dissolved in 100 grams of water to lower the freezing point 0.93°C? 100

41. A tenth of a gram-formula weight of a certain ionic substance, dissolved in 1000 grams of water, lowers the freezing point 3×0.186°C. What conclusion may be drawn?

42. How many moles of steam will be needed, and what actual weight of water will be condensed from it, during the steam distillation at 100°C of 1 mole of a substance that has a vapor pressure of 38 mm at that temperature (the vapor pressure of the steam being, of course, 760 mm). 200, 360

43. From a known fact about liquid and vapor at the critical temperature, explain why the heat of vaporization of a liquid is zero at its critical temperature.

44. Explain (§ 182) how one may calculate the actual number of molecules in a milliliter of a liquid of known density and molecular weight.

45. What is the osmotic pressure, in atmospheres, when 3.42 grams of cane sugar ($C_{12}H_{22}O_{11}$) is dissolved in 1 liter of solution, at 27°C? ($R = 0.0821$ liter-atmosphere per degree C per mole.) 246

46. If the walls of living cells are semi-permeable, explain why such cells swell and burst when placed in pure water, but shrivel when placed in a strong salt solution.

What name (p. 349) is given to solutions in which the cells display neither of these two opposite tendencies?

Chapter 23

THE SULFUR FAMILY

(Column 6A of the Periodic Table)

Symbol	Atomic Number		Formula	Melting Point (°C)	Boiling Point (°C)
O	8	Oxygen—colorless gas..........	O_2	−218	−182.7
S	16	Sulfur—yellow solid............	S_8	112.8	444.6
Se	34	Selenium—dark red or gray solid	Se_2	217	690
Te	52	Tellurium—silvery, brittle solid.	...	452	1400
Po	84	Polonium—radioactive metal....	...	....	....

301. General Characteristics of the Sulfur Family

With the elements of the sulfur family, as with the halogens, we notice a gradual alteration of physical properties, such as physical state and color, with increasing atomic number and consequent increase in atomic radius. With increasing atomic radius the outermost electrons of the atom are farther and farther from the nucleus, and so exert more attraction for neighboring atoms; this results in liquefaction, solidification, and eventually (with Se and Te) in the development, to a slight degree, of some of the physical properties of metals—for example, metallic luster and fair conductivity for heat and electricity.

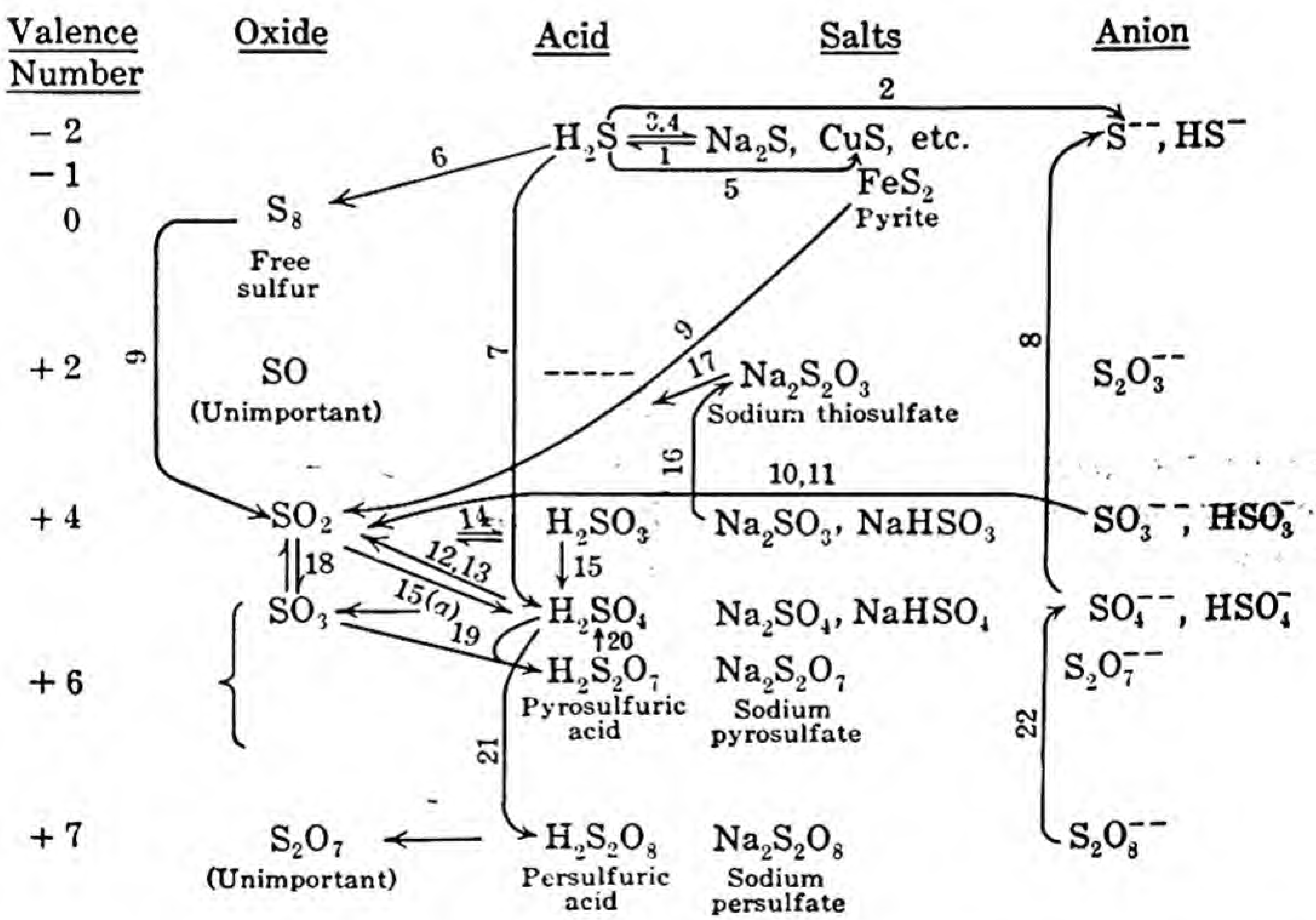
In their most important reactions the elements of the sulfur family (6 valence electrons) *gain 2 electrons or a share in 2 pairs of electrons* from other substances, to complete an outer octet of electrons. In this respect they are *typical non-metals*, though much less active than the halogens. As with the halogens, *increased atomic radius brings increased difficulty in acquiring and holding the extra electrons needed to form a complete octet.* In consequence, there is a gradual transition from the ionic state, in the *light metal oxides* (the ion O^{--}) to something intermediate between the ionic and covalent state, observed in the *heavy metal oxides*, and a typical covalent structure, observed in *heavy metal sulfides, selenides,* and *tellurides.* (Ex. 1, 2.)

302. Valence States of Sulfur, Selenium, and Tellurium

The chief valence states of sulfur and its most important reactions are shown in the accompanying table. We shall study these in some detail in the present chapter. The reactions of selenium and tellurium are similar except that the valence state +7 is unknown.

Thus in the valence state −2 we know hydrogen sulfide, H_2S; hydrogen selenide, H_2Se; and hydrogen telluride, H_2Te. These three compounds are alike in being colorless gases with an offensive odor.

In the valence state +4 we know the oxides SO_2, SeO_2, and TeO_2; the acids H_2SO_3, H_2SeO_3, and H_2TeO_3; and a few salts. In the valence state +6 we know the oxides SO_3, SeO_3, TeO_3; the acids H_2SO_4 and H_2SeO_4, and a few salts of the acid H_2TeO_4 (though not the acid itself).



The compounds of selenium and tellurium are in general more readily decomposed than those of sulfur. The acids are distinctly less active than the corresponding sulfur acids, and tellurium even plays the part of a metal in a few hydroxy-salts. (Ex. 3, 4.)

Geologic agencies, working over the elements of the earth's crust, during uncounted ages past, have reacted with similar elements in similar ways and so have tended to accumulate them in the same deposits. Selenium and tellurium therefore chiefly occur as impurities

in sulfide ores and sometimes even in free sulfur. They are far less abundant than sulfur, just as this is far less abundant than oxygen.

303. Occurrence of Sulfur

Sulfur makes up but a mere trace of the earth's crust; yet in most parts of the world there are enormous deposits of sulfur minerals. Free sulfur is often found in volcanic regions, as the result of reaction of sulfur dioxide with other gases issuing from volcanoes. The world's largest deposits of free sulfur are those in Louisiana and Texas. These are mined by *superheated water* (water heated, under pressure, above its normal boiling point), introduced through pipes to the desired depth. The sulfur is thus melted, then forced to the surface by compressed air.

Many of the most important metals are derived from sulfide ores. Zinc sulfide (zinc blende, ZnS) and lead sulfide (galena, PbS) are the most important sources of these two metals. Copper pyrites (chalcopyrite, $CuFeS_2$) is an important ore of copper. Iron pyrites (pyrite, FeS_2) is of no use as an ore of iron, but until recently has been the chief raw material for the manufacture of sulfuric acid. (Ex. 5, 6.)

The most plentiful mineral containing both sulfur and oxygen is gypsum (calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$). This is used for the preparation of plaster of paris, § 535. Barium sulfate ($BaSO_4$) is mined on a large scale for the manufacture of cheap white paint and for giving weight to silk fabrics.

Sulfur is of interest as one of twelve or more elements necessary for the life and growth of plants and animals. As a constituent of organic compounds, it is very widely distributed in small amounts in plant and animal matter, for example, in the yolk of eggs, many seeds, hair, and in the brain and nervous tissue. Organic sulfur compounds and hydrogen sulfide in petroleum and natural gas offer serious problems, owing to corrosion by sulfuric acid formed by their combustion. American sulfur is above 99.5 per cent pure, the most objectionable impurity being a trace of petroleum oil, which often prevents it from burning freely on stationary grates.

304. Allotropic Forms of Sulfur

Sulfur is one of many substances, including both elements and compounds, that are capable of existing in several different crystalline forms. Such substances are said to be *polymorphic*.

Polymorphic elements are said to be *allotropic*. The different crystalline or (sometimes) liquid or gaseous forms of such an element

are frequently referred to as the *allotropic forms* of the element. Sulfur, carbon, oxygen, phosphorus, iron, arsenic, selenium, tin, antimony, tellurium, and boron are conspicuously allotropic; most of the heavy metals (with the exception of mercury) show some evidence of allotropic modifications.

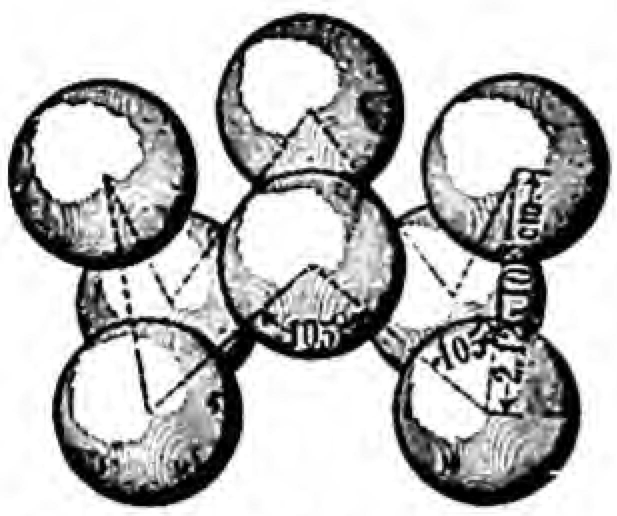


FIG. 112. Molecule of sulfur, S_8.

X-ray research has shown that the sulfur molecule in crystalline sulfur is a ring of 8 atoms, S_8, shown in Fig. 112. This molecule is the structural unit in building the space lattice of ordinary crystalline sulfur, known as *rhombic sulfur* (Fig. 113). Rhombic sulfur is readily obtained by the evaporation of a solution of sulfur in carbon disulfide. It is the stable form of sulfur, at temperatures below 96°C.

The same structural unit, S_8, repeated in a different space pattern, results in *monoclinic sulfur* (Fig. 114), which crystallizes in long needles. Monoclinic sulfur is readily obtained by melting rhombic sulfur (m.p. 112.8°), pouring it into a folded filter paper in a funnel, permitting it to cool until partly solidified, then perforating the solid crust and pouring away the part that still remains liquid.

FIG. 113. Crystals of rhombic sulfur.

FIG. 114. Crystals of monoclinic sulfur.

From 96°C up to the melting point of monoclinic sulfur, 119°C, the monoclinic form is stable. Evidently 96°C is the *transition temperature*, at which the rhombic and monoclinic forms may remain indefinitely in equilibrium:

$$\underset{\text{Density 2.07}}{S_8\ (\text{rhombic})} \underset{96°\text{C}}{\rightleftharpoons} \underset{\text{Density 1.96}}{S_8\ (\text{monoclinic})}$$

Finely powdered, apparently amorphous (but doubtless *microcrystalline*) sulfur, often called *flowers of sulfur*, is produced whenever

sulfur vapor is suddenly cooled; and various forms of colloidal sulfur have been made in different ways.

Sulfur melts to a limpid, amber-colored liquid (Sλ) in which the S_8 rings still maintain their identity. As this liquid is heated to higher temperatures it begins to darken and thicken rapidly in the range 160°C to 180°C, and at the latter temperature is of a deep reddish brown color and of a rubbery consistency. This change probably consists in the breaking of the S_8 rings to produce filaments of sulfur, which then become tangled or interlocked, thus enormously increasing the viscosity of the material. The chief component of this highly viscous liquid (Sμ) differs from Sλ in being but slightly soluble in carbon disulfide.

Liquid sulfur boils at 444.6°C, the vapor at that temperature consisting chiefly of S_8 molecules. At higher temperatures it gradually dissociates, forming S_4, S_2, and ultimately, at 2000°C, simple monatomic molecules, S. (Ex. 7.)

305. Preparation and Physical Properties of Hydrogen Sulfide (Illustrating the Preparation of a Volatile Acid, § 165)

Hydrogen sulfide (formerly called sulfureted hydrogen) is a colorless, readily liquefiable, fairly soluble, *poisonous* gas of offensive odor. It occurs in nature whenever plant or animal matter decays in a limited supply of air.

The "sulfur waters" of mineral springs, in many parts of the world, owe their odor and taste to hydrogen sulfide. (Ex. 8.) It is also often found in natural gas, sometimes in such large amounts as to make the gas unfit for use unless means are taken to remove it. Coal gas and the gas liberated in *cracking processes* for converting petroleum into gasoline (§ 460) also usually contain small amounts of hydrogen sulfide, until purified. In all these, the hydrogen sulfide is derived from organic sulfur compounds of plant or animal material.

Hydrogen sulfide may be prepared *by the interaction of any dilute, non-oxidizing acid of reasonable activity with a metallic sulfide:*

Equation 1: $$\underset{\text{An acid}}{2H^+} + \underset{\text{A sulfide}}{S^{--}} \rightarrow H_2S\uparrow$$

Ferrous sulfide, FeS, is generally used. Pyrite, FeS_2, will not react with dilute acids unless a strong reducing agent, such as zinc, is present. (Ex. 9.)

Hydrogen sulfide is also often prepared in the laboratory by heating a mixture of paraffin and sulfur, with asbestos fiber to increase the

porosity of the mixture. It may now be purchased in strong steel cylinders, liquefied by pressure.

It is not practical to prepare hydrogen sulfide by direct union of hydrogen and sulfur, for at temperatures sufficiently high to bring about rapid direct union we find that hydrogen sulfide is decomposed. In other words, we have to deal with a reversible reaction.

$$H_2 + S \rightleftharpoons H_2S$$

306. Hydrogen Sulfide as an Acid

Hydrogen sulfide, in solution in water, is slightly ionized, reacting with water in two stages:

Equation 2: $$\underbrace{H_2S + H_2O}_{H^+} \rightleftharpoons H_3O^+ + HS^-$$
$$\underbrace{HS^- + H_2O}_{H^+} \rightleftharpoons H_3O^+ + S^{--}$$

Thus a solution of hydrogen sulfide is to be considered as containing not only H_2S *molecules* but also a few *acid sulfide ions*, HS^-, and a still smaller number of *sulfide ions*, S^{--}. Since the transfer of H^+ from H_2S molecules to water is far from complete we recognize hydrogen sulfide as a *slightly active* acid.

The acid properties of hydrogen sulfide are also made evident by its forming two series of salts:

1. If it is passed into a solution of an alkali or soluble carbonate until this is saturated, we have an excess of hydrogen sulfide, and an *acid sulfide* is formed:

Equation 3: $$NaOH + \underset{\text{(Excess)}}{H_2S} \rightarrow \underset{\substack{\text{Sodium}\\\text{hydrogen}\\\text{sulfide}}}{NaHS} + H_2O$$

or, as an ionic equation:

Equation 3(*a*): $$OH^- + H_2S \rightarrow HS^- + H_2O$$

2. By adding an alkali to a solution of an acid sulfide, or by using an excess of an alkali with hydrogen sulfide, the result is a *normal sulfide:*

Equation 4: $$\underset{\text{(Excess)}}{2NaOH} + H_2S \rightarrow \underset{\substack{\text{Sodium}\\\text{sulfide}}}{Na_2S} + 2H_2O$$

or, as an ionic equation:

Equation 4(*a*): $$2OH^- + H_2S \rightarrow S^{--} + 2H_2O$$

(Ex. 10.)

307. Hydrogen Sulfide as a Precipitant

Hydrogen sulfide is an important precipitant. It reacts with salts of most of the heavy metals, to produce *insoluble sulfides*, many of them with *characteristic colors.* For this reason hydrogen sulfide is useful *in identifying heavy-metal cations*, and is an important laboratory reagent for this purpose, in spite of its offensive odor and the *danger* that is involved in its being poisonous. Precipitation of insoluble sulfides probably comes about through the formation of *acid sulfides*, which then decompose:

Equation 5: $Cu^{++} + 2HS^{-} \rightarrow Cu(HS)_2 \rightarrow CuS\downarrow + H_2S$

By writing this equation as

Equation 5(*a*): $Cu^{++} + H_2S \rightarrow CuS\downarrow + 2H^{+}$

we emphasize that nearly all the hydrogen sulfide, at any given moment, exists as molecules rather than as ions. (Ex. 11.)

Most insoluble metallic sulfides, after precipitation by hydrogen sulfide as just described, may be redissolved by adding an acid to the liquid in which they are suspended:

$$CuS + 2H^{+} \rightarrow Cu^{++} + H_2S\uparrow$$

This is the exact opposite of the preceding reaction, by which the insoluble sulfide was first precipitated. A mixture of precipitated sulfides may sometimes be separated by treating it with an acid of properly chosen concentration or activity, to dissolve one sulfide and leave another undissolved. Or, by passing hydrogen sulfide into a solution of carefully chosen acidity, certain metals may be precipitated and others left unprecipitated.

308. Hydrogen Sulfide as a Reductant

Hydrogen sulfide is an important reductant.

1. Mild oxidants, such as air and dilute nitric acid, oxidize it to free sulfur and an acid (H^{+}) or water:

Equation 6: $H_2S \rightarrow S^{\circ} + 2H^{+} + 2e$

2. In the presence of vigorous oxidants, such as hot nitric acid of fair concentration, it is oxidized to a sulfate or sulfuric acid:

Equation 7: $H_2S + 4H_2O \rightarrow SO_4^{--} + 10H^{+} + 8e$

As valence state equations (§ 266) the two preceding reactions would be written:

Equation 6(*a*): $S^{--} \rightarrow S^{\circ} + 2e$

Equation 7(*a*): $S^{--} \rightarrow S^{+6} + 8e$

The student should pause now to work out equations for a few reactions illustrating the three chemical properties of hydrogen sulfide that are listed in this and the two preceding sections. (Ex. 12–17.)

309. Sulfides and Polysulfides

The sulfates of alkali and alkaline-earth metals, on being strongly heated with powdered charcoal, are reduced to sulfides:

Equation 8: $\underset{\text{Sodium sulfate}}{Na_2SO_4} + 4C \rightarrow \underset{\text{Sodium sulfide}}{Na_2S} + 4CO \uparrow$

Most heavy-metal sulfates, treated in the same way, would yield the metal.

A solution of sodium sulfide, prepared as just described, is the active reagent in the preparation of Kraft paper from southern pine and other woods. The same reaction occurs in the preparation of sodium hydroxide (and formerly sodium carbonate) by the famous Leblanc process.

Sulfides and hydroxides of the alkali metals (Na, K, NH_4) and alkaline-earth metals (Mg, Ca, Sr, Ba) react with sulfur to form polysulfides. Lime-sulfur spray, used in combating fungus enemies of plants, is a red solution, made by boiling a suspension of slaked lime with sulfur. It contains a mixture of the calcium polysulfides, CaS_4 and CaS_5. When this solution is poured into dilute acids, an unstable yellow oil separates, which by fractional distillation in a vacuum yields H_2S_2 and H_2S_3. These substances slowly decompose into hydrogen sulfide and free sulfur. (Ex. 18.)

310. Preparation of Sulfur Dioxide

Most of the commercially important compounds of sulfur are derived from sulfur dioxide. This is usually prepared:

1. *Commercially*, on an enormous scale, by burning sulfur, or by heating a sulfide mineral such as pyrite, FeS_2, in a current of air:

Equations 9: $S + O_2 \rightarrow SO_2 \uparrow$

$$2FeS_2 + 5\tfrac{1}{2}O_2 \rightarrow Fe_2O_3 + 4SO_2 \uparrow$$

Vast quantities of sulfur dioxide are produced as a by-product in *roasting* sulfide ores of copper, lead, and zinc, preliminary to *smelting* these ores for the recovery of metal.

2. *In the laboratory*, by the reaction of a sulfite or an acid sulfite with an acid:

Equation 10: $SO_3^{--} + 2H^+ \rightarrow SO_2\uparrow + H_2O$

Equation 11: $HSO_3^- + H^+ \rightarrow SO_2\uparrow + H_2O$

3. *As a lecture demonstration*, often by heating an oxidizable element, such as sulfur, zinc, or iron, with concentrated sulfuric acid:

Equation 12: $2H_2SO_4 + Fe \rightarrow FeSO_4 + SO_2\uparrow + 2H_2O$

Equation 13: $2H_2SO_4 + S \rightarrow 3SO_2\uparrow + 2H_2O$

This reaction incidentally reveals concentrated sulfuric acid as a vigorous oxidizing agent. (Ex. 19, 20.)

311. Physical Properties of Sulfur Dioxide

Sulfur dioxide is a *colorless gas* with the *pungent odor* of burning sulfur. It is *readily liquefied*, even at room temperatures, by slight pressures (4 atmospheres at 25°C). It is an excellent *solvent* for waxes, resins, and many other classes of organic substances, and is a selective solvent in an important process for improving the quality of lubricating oil. The less desirable components of the lubricating oil are dissolved in liquid sulfur dioxide, and so are removed.

Liquid sulfur dioxide has been widely used as a refrigerant, but is being displaced by fluorine compounds already described (§ 281).

312. Chemical Properties of Sulfur Dioxide and Sulfurous Acid

The chief reactions of sulfur dioxide are:

1. It combines reversibly with water to form sulfurous acid:

Equation 14: $SO_2 + H_2O \rightleftharpoons H_2SO_3$

This acid, like hydrogen sulfide, forms two series of salts, the *acid sulfites*, containing the anion HSO_3^-, and *normal sulfites*, containing the anion SO_3^{--}. (Ex. 21.)

2. Solutions of sulfur dioxide or of sulfurous acid are important *reducing agents*, being themselves oxidized to sulfuric acid:

Equation 15: $SO_3^{--} + H_2O \rightarrow SO_4^{--} + 2H^+ + 2e$

As a valence state equation this would appear:

Equation 15(*a*): $$S^{+4} \rightarrow S^{+6} + 2e$$

Liquid sulfur dioxide, free from water, is not a reducing agent, for even bromine and iodine can be dissolved in it and recovered, unchanged.

313. Uses of Sulfurous Acid and Its Salts

1. Solutions of sulfurous acid are frequently used for bleaching silks, sponges, hair, wool, and straw. All these materials would be injured if bleached by chlorine.

2. Solutions of sulfurous acid are useful *disinfectants* and *germicides*, probably owing to their having sufficient acidity to discourage the growth of microorganisms, and because they combine with and hence exclude atmospheric oxygen. In the preparation of corn starch from corn the grain is soaked for several days in dilute sulfurous acid, which prevents fermentation. The bleaching of fruit by exposure to sulfur dioxide, previous to drying, is in part accomplished by preventing discoloration by enzymes and microorganisms.

Sulfites and *acid sulfites* are important *reducing agents*. They have some applications in the preparation of dyestuffs and in photography. Calcium acid sulfite, $Ca(HSO_3)_2$, is made by passing an excess of sulfur dioxide into a suspension of slaked lime, $Ca(OH)_2$. This solution is used on a grand scale in the preparation of paper pulp from wood by the so-called *sulfite process* (§ 466).

314. Thiosulfates

Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, is commonly called "hypo."[1] A solution of this salt is an excellent solvent for silver salts that are insoluble in water, and is used for this purpose in photography as a *fixing bath*. There are two important methods for the preparation of sodium thiosulfate:

1. By dissolving powdered sulfur in a hot solution of sodium sulfite:

Equation 16: $$Na_2SO_3 + S \rightarrow Na_2S_2O_3$$

2. Calcium thiosulfate is formed by slow oxidation of calcium polysulfide (§ 309) on exposure to air. From this solution, by reaction with sodium carbonate, sodium thiosulfate may be prepared.

[1] This is not to be confused with sodium dithionite, $Na_2S_2O_4$, which has often incorrectly been termed sodium hyposulfite.

A solution of sodium thiosulfate is an important reagent in the laboratory. *It reacts with iodine to form sodium tetrathionate:*

Equation 17: $2Na_2S_2O_3 + I_2 \rightarrow \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6} + 2NaI$

It is oxidized by chlorine, being converted into sodium sulfate. This reaction makes sodium thiosulfate of importance in the bleaching industries and elsewhere *as a means for removing traces of free chlorine* that might otherwise remain in a product treated with chlorine. (Ex. 22.)

315. Sulfur Trioxide. The Contact Process

Sulfur trioxide is a colorless liquid, which freezes at 16.8°. The solid thus obtained is readily converted into other crystalline forms, melting respectively at 32.5° and 62.2°C. All three solids and the liquid yield vapor of the formula SO_3.

In contact with a catalyst, sulfur dioxide readily combines with a further quantity of oxygen, to form sulfur trioxide:

Equation 18: $2SO_2 + O_2 \rightleftharpoons 2SO_3 + 45.2$ kilocalories

An excess *of air or oxygen* is needed to secure a reasonably complete conversion of the sulfur dioxide into sulfur trioxide. The reaction is most nearly complete at *low temperatures.* But since too low a temperature would make the reaction too slow, an intermediate temperature (about 400°C) is employed with a *catalyst* to insure that the reaction shall promptly attain equilibrium.

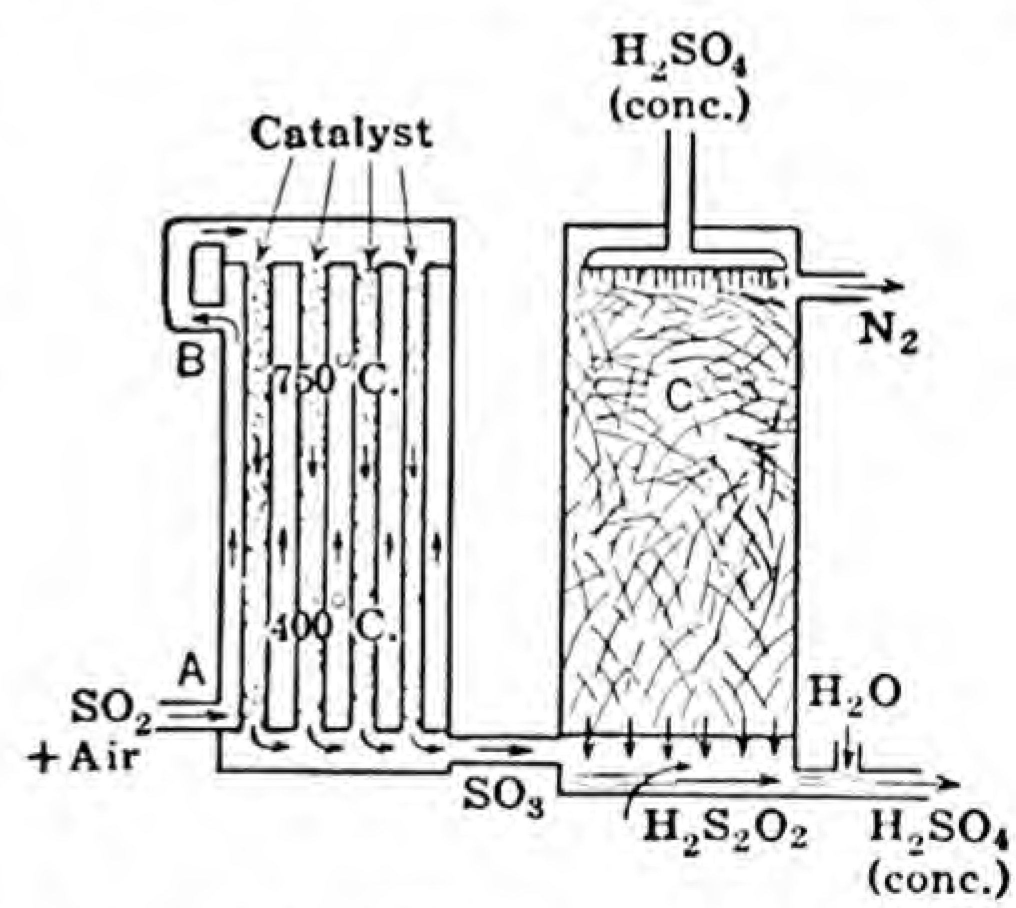


FIG. 115. The contact process for manufacturing sulfuric acid. Observe that the incoming mixture of sulfur dioxide and air is preheated by being passed around the tubes containing the catalyst, and in which heat is being liberated by the reaction. The reaction is begun at about 750°C, then finished at about 400°C, since it is more nearly complete at the lower temperature.

The catalyst first employed in the contact process, about 1900, was platinum, distributed as a thin coating of finely divided metal (platinum black) over asbestos or other porous material. This long remained the most widely used catalyst, in spite of its great cost and

its tendency to be "poisoned"—rendered inactive after brief service—by traces of arsenic and other impurities in the sulfur dioxide (§ 329). Ferric oxide, mixed with cupric oxide, has often been used as a catalyst, and certain mixtures containing vanadium oxide not only are extremely effective catalysts but also are nearly immune to poisoning. Thus the need for a costly preliminary purification of the sulfur dioxide gas is done away with and the vast quantities of impure sulfur dioxide, a by-product of roasting sulfide ores in a current of air, are made more easily available for the manufacture of concentrated sulfuric acid by the contact process.

Sulfur trioxide combines directly with water to form sulfuric acid. In commercial practice, to avoid the production of a fog of liquid droplets of sulfuric acid, it has been found best to dissolve the sulfur trioxide in concentrated sulfuric acid rather than in water:

Equation 19: $$SO_3 + H_2SO_4 \rightarrow \underset{\text{Pyrosulfuric acid}}{H_2S_2O_7}$$

Then, by diluting the pyrosulfuric acid, ordinary concentrated sulfuric acid is obtained:

Equation 20: $$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

316. Preparation of Sulfuric Acid

The substance represented by the formula H_2SO_4, properly called *hydrogen sulfate*, is a colorless, oily liquid, which freezes at 10.49°C. Solutions of this in water are called *sulfuric acid.* The concentrated acid has a density of 1.835 g/ml and contains about 96 per cent hydrogen sulfate. (Ex. 23.)

Sulfuric acid is prepared from sulfur dioxide (made by burning sulfur or by roasting pyrite, § 310). The *contact process*, described above, yields most of the concentrated acid of commerce.

Dilute sulfuric acid is usually made by the *chamber process*, in which sulfur dioxide is oxidized to sulfuric acid in roomy chambers or towers, through the agency of atmospheric oxygen, with oxides of nitrogen (NO_2 and N_2O_3) serving as a catalyst or *oxygen carrier.*

317. Chemical Properties of Sulfuric Acid

Concentrated sulfuric acid (consisting chiefly of the molecules, H_2SO_4) *is a vigorous dehydrating agent and oxidizing agent.* Both properties come into play when it carbonizes materials like sugar and paper. The residue is a porous black mass, largely carbon; yet the odor

of sulfur dioxide, always in evidence, is proof that the sulfuric acid has oxidized the material to a slight extent, and has been itself reduced.

Dilute sulfuric acid is a moderately active acid, transferring protons to water in two stages, as already described (§ 189). The reaction is so violent that the solution may actually boil; hence *one should always dilute sulfuric acid by pouring it into a large excess of water*, to minimize the increase in temperature. *Never pour water into the concentrated acid.*

The reactions of sulfuric acid are those of any other moderately active acid (review § 191). (Ex. 24.)

318. Uses of Sulfuric Acid

The chief industrial countries of the world use vast quantities of sulfuric acid every year—over 8,000,000 tons, reckoned as 62 per cent acid, in the United States alone, in 1937. The student should attempt to remember something of *the manner of its use*, in a number of different industries:

1. In *the fertilizer industry*, for the production of ammonium sulfate, by direct combination with ammonia, and for the manufacture of *superphosphate fertilizer* (§ 388). In the United States this accounts for about a fourth of the sulfuric acid used.

2. In *refining petroleum*. Crude petroleum contains dark-colored, tarry substances, which may be dissolved and so removed by agitating the petroleum with sulfuric acid. The acid sludge is drawn off and discarded, and the petroleum washed and distilled. This use accounts for about 15 per cent of the sulfuric acid employed in the United States.

3. In the manufacture of chemical products, particularly *other acids*, by reaction of sulfuric acid with their salts; *ether*, by reaction of sulfuric acid with alcohol; and many *sulfates*, such as copper sulfate, aluminum sulfate, and ferrous sulfate, by reaction of sulfuric acid with metals or metallic oxides.

4. In the manufacture of *dyes* and *medicinal substances* from coal tar (12.5 per cent of sulfuric acid used in United States).

5. In *pickling steel;* the oxide film is cleaned off by dipping the steel into dilute sulfuric acid, as a preliminary to galvanizing or enameling.

6. In *winning metals from their ores* (metallurgy). Certain ores of copper and zinc may be extracted directly with sulfuric acid. Zinc is sometimes prepared from such solutions by electrodeposition; and copper, regardless of how it is prepared, is finally purified by electrolysis in a bath acidified with sulfuric acid (§ 522).

7. In the *manufacture of paints and pigments.*

8. In the *manufacture of explosives*, such as dynamite, smokeless powder, and the nitrate and nitro compounds which form two important groups of explosives (§ 381).

9. In the manufacture of *nitrocellulose films* and *lacquers* (§ 467), in the textile industry for scouring wool and *neutralizing alkali* used in the purification of cotton and linen fibers. *Rayon* is produced by several different processes, which usually require sulfuric acid for neutralizing alkali at some stage. Rubber is reclaimed from tires with the aid of dilute sulfuric acid.

319. Persulfuric Acid and Persulfates (Illustrating Electrochemical Oxidation, § 260)

When an electric current is passed through concentrated sulfuric acid, cooled in ice, with a diaphragm to keep the products at the two electrodes from coming into contact, hydrogen gas is produced at the cathode and persulfuric acid at the anode:

$$\text{Equations 21:} \begin{cases} 2H_2SO_4 + 2e \rightarrow 2HSO_4^- + H_2\uparrow & \text{(Cathode)} \\ 2H_2SO_4 \rightarrow \underset{\text{Per (di)-sulfuric acid}}{H_2S_2O_8} + 2H^+ + 2e & \text{(Anode)} \end{cases}$$

This is the first step in the preparation of *hydrogen peroxide*, commercially. The second step is hydrolysis of the persulfuric acid, to yield sulfuric acid and hydrogen peroxide. Persulfuric acid may also be produced by the interaction of hydrogen peroxide and chlorosulfonic acid, $SO_2(OH)Cl$. It is a white, crystalline solid, melting at 45°C.

Potassium persulfate and ammonium persulfate are slightly soluble salts, which may be produced from persulfuric acid or by the electrolysis of cold concentrated solutions of potassium acid sulfate or ammonium acid sulfate.

Persulfuric acid itself and its salts are *vigorous oxidizing agents*, being thereby reduced to sulfuric acid or a sulfate.

$$\text{Equation 22:} \quad \underset{\text{Persulfate ion}}{S_2O_8^{--}} + 2e \rightarrow \underset{\text{Sulfate ion}}{2SO_4^{--}}$$

320. Selenium and Tellurium

Small quantities of *selenium* found in pyrite, FeS_2, are recovered from the dust flues of sulfuric acid plants that use pyrite as a raw material. Selenium and tellurium in sulfide ores of copper find their

way into the impure copper produced by smelting these ores, and are finally recovered from the anode mud which is obtained as a by-product in refining crude copper by electrolysis (§ 522).

Selenium, like sulfur, occurs in several different allotropic forms, including an amorphous dark-red powder, soluble in carbon disulfide, and a lead-gray crystalline form, with a metallic luster. The crystalline form is obtained by the slow cooling of melted selenium and is insoluble in carbon disulfide. Its conductivity for electricity is very greatly increased by exposure to light. This property has been used in a delicate *photometer* for measuring the intensity of the light from individual stars; but since the response to light is not instantaneous, selenium does not lend itself to recording sound on film, in competition with photoelectric cells that are based on the emission of electrons by an alkali metal (§ 179), rather than on variations in conductivity with variations in intensity of illumination.

Rubber containing selenium is resistant to abrasion and is employed as a fire-resistant covering for electric cables. Small traces of selenium, added to glass, neutralize any greenish tinge that may result from traces of iron, and large quantities result in a ruby-red glass, used in signaling (stop-lights) or for decorative purposes.

Certain areas of grazing land in western states contain so much selenium in the soil, and thence accumulated in grass and field crops, that animals are poisoned. A few wells are poisonous for the same reason. As such areas are recognized they are closed to agriculture.

Tellurium is metallic in its appearance, and is a fair conductor of heat and electricity, but in chemical behavior occupies an intermediate position between metals and non-metals. It has no important use, though lead is sometimes alloyed with small quantities of tellurium to increase its resistance to corrosion and improve its tensile strength.

Technical Words

Superheated water—water heated above 100°C, boiling being prevented by retaining the liquid under pressure.

Polymorphic, p. 355. **Allotropic**, p. 355.

Allotropy—the occurrence of an element in two or more allotropic forms.

Transition temperature—the temperature at which two or more mutually intercovertible solids are in equilibrium, hence may remain in contact indefinitely, without any phase disappearing by being transformed into others. Sometimes a liquid or vapor phase is also present at the transition temperature.

Precipitant—a reagent entering into a reaction that results in a precipitate.

Metallurgy—the art of winning metals from their ores.

Roasting (a metallurgical term)—heating an ore in a current of air, to oxidize and volatilize sulfur, arsenic, and other undesirable elements.

Smelting—any process of melting or fusion, for recovering metals from their ores.

Selective solvent—a solvent that dissolves one ingredient of a mixture, leaving others practically undissolved.

Oxygen carrier—a catalyst that acts by combining with oxygen to form an unstable compound, which then yields oxygen to an oxidizable substance.

Photometer—an instrument for measuring the energy intensity of light or its *visual intensity*, namely its effect on the human retina. An instrument that measures the energy intensity of radiant energy, including invisible light, emitted by a heated body, is usually called a *radiometer*.

Exercises

1. What ions are present in sodium oxide and sodium peroxide, respectively?

2. Show how an atom of sulfur, by sharing electrons, produces a molecule of hydrogen sulfide.

3. Which of the valence states indicated for sulfur in the table in § 302 are also known for oxygen?

4. Show that sulfur in the persulfate ion really has the valence number indicated in the table in § 302.

5. Since the iron in pyrite is ferrous iron, what must the anion be? To what anion of a related element, already studied, does this correspond?

6. When galena is roasted in a current of air it is in part converted into lead sulfate. Then, when this is heated, even in the absence of air, with unchanged galena, sulfur dioxide escapes and metallic lead separates. Write and balance the two equations here indicated.

7. Estimate the density of sulfur vapor at its boiling point, in comparison with air at the same temperature. 883

8. Free sulfur is sometimes deposited by sulfur springs, owing to oxidation of dissolved gas by oxygen of the atmosphere. Write an equation.

9. Ferrous sulfide is commonly made by heating sulfur with an *excess* of iron filings. Then what *two* gases will be liberated by treating the material so prepared with dilute acid?

10. What volume of normal alkali solution reacts with 22.4 liters of hydrogen sulfide gas under standard conditions, in forming an acid sulfide and in forming a normal sulfide, respectively?

11. A 1-gram sample of an aluminum alloy, on being dissolved in acid, then saturated with hydrogen sulfide, yields 95.5 mg of cupric sulfide. What percentage of copper is contained in the alloy? 635

12. Write an equation for the reaction that takes place when an excess of hydrogen sulfide is passed into lime water, $Ca(OH)_2$.

13. Write ionic equations for the final result when hydrogen sulfide is used in precipitating silver, cadmium, and antimony (Sb^{+3}) from solutions containing soluble salts of these elements.

14. Write an ionic equation for the action of hydrogen sulfide in reducing a ferric salt (ferric ion) to the ferrous condition.

15. Write an equation for the reaction to be expected when hydrogen sulfide is bubbled through water in which finely powdered iodine is suspended.

16. Give an ionic equation, balanced by the ion-electron method (§ 265) for the reaction of hydrogen sulfide with a dichromate in an acid solution.

17. Show how the reaction just considered may be written and balanced as a valence state equation.

18. Write an equation to show how calcium tetrasulfide may be converted into sodium tetrasulfide, calcium carbonate being precipitated.

19. When sulfur is oxidized by heating with concentrated sulfuric acid, both reactants yield sulfur dioxide. Determine what total volume of sulfur dioxide, under standard conditions, may be obtained for each gram atom of sulfur. 672

20. How many moles and what volume of sulfur dioxide gas are set free by the action of an excess of acid on one mole of sodium sulfite? 100, 224

21. Write an equation for the reaction of sulfur dioxide with an excess of ammonium hydroxide solution. What salt is produced if a further quantity of sulfur dioxide is added, until sulfurous acid is present in a large excess?

22. What is the valence number of sulfur in sodium tetrathionate?

23. How many moles of hydrogen sulfate are contained in 1 liter of the concentrated acid, density 1.84 g/ml, containing 96 per cent hydrogen sulfate by weight? What is the normality of the concentrated acid? 177, 353

24. Write equations showing how a limited amount of sulfuric acid, also an excess of sulfuric acid, will react with sodium carbonate. Write the corresponding ionic equations.

Chapter 24

REACTION RATE

321. Slow and Rapid Reactions

In the applications of chemistry to practical affairs we are interested not only in the *identity* of the products that a chemical reaction may produce, but also in the *rate* at which it takes place. Dynamite would not be very useful if its decomposition into gaseous products were not practically instantaneous. On the contrary, we seek to retard or prevent the chemical reactions responsible for the destruction of fabrics or rubber when exposed to the air and sunlight, or for the corrosion of metals in the presence of air and moisture.

By *reaction rate* we mean the rate at which some stated reactant is transformed or some stated resultant is produced. It is usually expressed as the number of *moles* or *molecules* transformed or produced in *unit volume* of the reaction mixture, during *one minute* or *one hour* of time.

Some reactions are completed *instantaneously.* Examples are (1) the neutralization of an acid by a base, or (2) the interaction of two dissolved salts to produce a precipitate.

Reactions involving oxidation and reduction, on the contrary, often require measurable time for their accomplishment. Many of the important reactions of organic chemistry are so slow that they are commonly brought about by heating the reactants together at a high temperature for many hours. Reactions that take place in vitreous materials or at the bounding surfaces of solids may require years for their accomplishment.

Whether a reaction is very slow or rapid, it may eventually become practically *complete;* or it may remain incomplete because it finally reaches a condition of *equilibrium*, in which it is exactly canceled by a reaction that proceeds at the same rate in the opposite direction

322. Factors Determining Reaction Rate

Reaction rate in general is determined by:

1. *The nature of the reactants.* Those that react most rapidly under given conditions are said to be *active* (active acids and bases, for example, as compared with slightly active ones).

2. *The state of subdivision of the reactants.* Chemical reactions between different substances can, of course, take place only at the surfaces at which they come in contact. When two substances are finely divided and intimately mixed they present more surface to each other, and thus react more rapidly than coarser material.

Solutions react even more rapidly, for here the process of subdivisioning has been continued down to the individual molecules or ions of the dissolved substance. The finely powdered ingredients of baking powder, if kept dry, will remain in contact with each other for years, without noteworthy change; but when water is added there is violent reaction, liberating carbon dioxide gas.

3. *The temperature.* Reactions proceed more rapidly as the temperature is increased. The housewife keeps milk in a refrigerator, to decrease the rate of the reactions that result in the souring of milk; but she sets dough in a warm place, to increase the rate of the reactions carried out by the yeast, producing carbon dioxide, to cause the dough to rise. Every amateur photographer understands that the length of time that it takes to develop a photographic film depends on the temperature of the developing solution, and is very much shortened by even a slight increase in temperature.

Though a reaction is practically always made more rapid by a slight increase of temperature, (1) it may become less nearly complete; or (2) *secondary reactions* (p. 383) may appear at the higher temperature and decrease the yield; or (3) too high a temperature may at times destroy or restrain some living organism, enzyme (p. 382), or catalyst, responsible for the progress of the reaction.

4. *The nature of the solvent or the presence of a catalyst* (§ 327). Certain organic reactions proceed a thousand times as fast in solution in anhydrous ethyl alcohol as they do in aqueous solutions.

5. *The particle concentration of each reactant, i.e.*, the number of reacting particles (molecules or ions) in unit volume. This applies only to reactions in which the reactants are present in a homogeneous mixture or true solution—gaseous, liquid, or solid. Doubling the concentration of any reactant then doubles or more than doubles the reaction rate.

6. Many reactions are accelerated by *radiant energy*, including ordinary visible light, ultraviolet light, and X-rays. Examples are the decomposition of hypochlorous acid into hydrochloric acid and free oxygen (§ 205); the frequently explosive union of chlorine and hydrogen (§ 335); the photosynthesis of starch in the leaves of green plants; and the photographic arts (§ 569).

323. Photochemical Reactions

Reactions in which light initiates or accelerates chemical reactions are often called *photochemical reactions*. They have been actively studied during more than a century. When light passes through any material we find that certain frequencies or wavelengths are *absorbed*, others being *transmitted*, almost undiminished. Only the absorbed frequencies have any effect on the reaction rate. This is evidently because the absorbed radiant energy *activates* certain molecules (renders them capable of reacting). These may then decompose or are otherwise chemically altered.

Radiant energy behaves as if it consisted of small, indivisible units of energy, analogous to the practically indivisible atoms that compose ordinary matter. These "particles" of radiant energy are called *photons* or *quanta*. An incandescent body, emitting light, is shooting photons out in all directions, one after another, in an endless stream. This view of the nature of radiant energy does not supersede the wave theory of light, since photons, in their flight through space or in their passage through transparent materials, behave as if guided by electromagnetic waves.

The energy possessed by a single photon is proportional to the *frequency* (complete vibrations per second) of the accompanying electromagnetic wave. Representing the frequency by ν (*Greek:* nu) the energy of one photon is $h\nu$, in which h is Planck's constant, which has the numerical value 6.624×10^{-27} erg-second.

Einstein (1912) conceived of photochemical reactions as being accomplished by the collisions of individual quanta of radiant energy with individual molecules. The whole energy of one quantum would then be absorbed by one molecule, which would thus often be activated (rendered capable of reacting). In brief, *the initial effect, in any chemical process induced by light, is the absorption of one quantum of energy by an individual molecule* (Einstein's Photochemical Law). The molecule thus activated may then either *react* (transforming one or more other molecules) or in some way may be *deactivated*, without reacting.

324. Three Ways in Which a Molecule May Become Activated

Whenever two substances are intimately mixed, as in a gaseous or liquid solution, the irregular motion of their molecules brings every molecule of either substance into collision with molecules of the other substance, *millions of times each second!* Many reactions are nevertheless very slow. This proves that *molecules ordinarily do not react when they collide, even when their chemical nature is such as to favor reaction.* A molecule of a substance A may collide with molecules of another substance, B, many millions of times, rebounding on each occasion without being chemically altered; yet the very next collision may result in a union of the two to form the compound AB, or in some other chemical change.

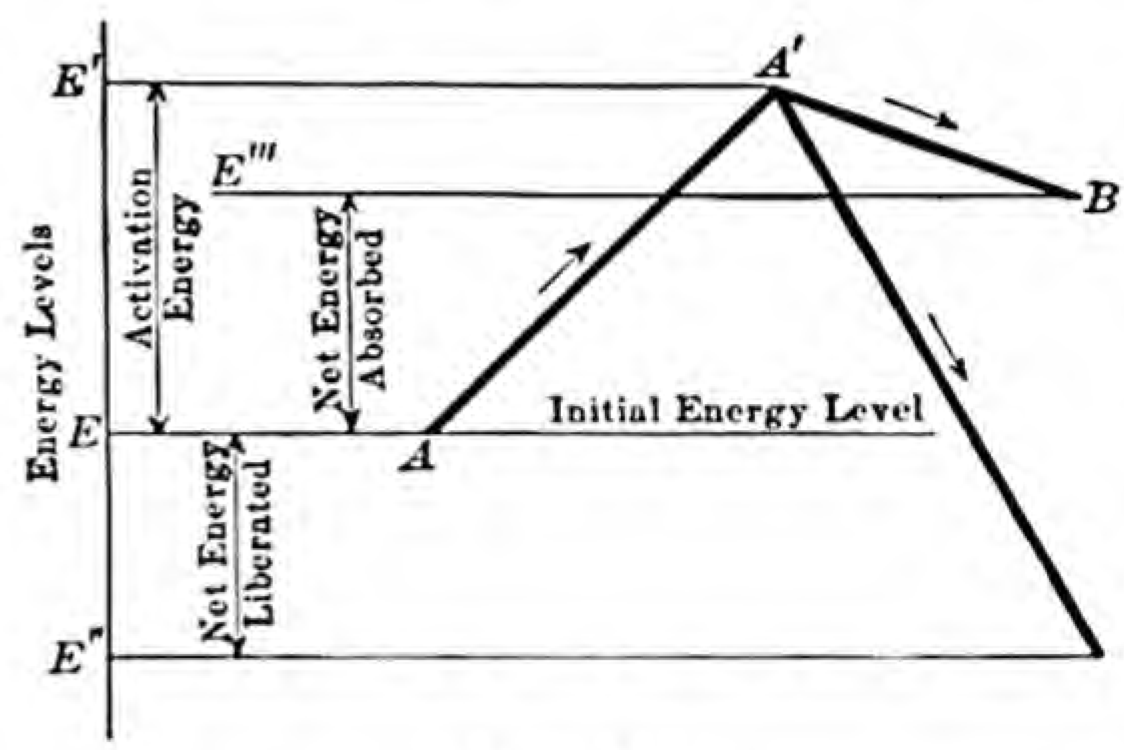


FIG. 116.

Further consideration leads us to conclude that *colliding molecules do not react unless at least one of them is possessed of an unusual amount of energy for a molecule at that temperature*—in other words, exists in what is called an *activated state.*[1]

Since the neutralization of an acid by a base and the direct union of ions to form a precipitate are accomplished instantaneously, *we may regard ions as being activated molecules.* Electrically neutral molecules, by contrast, must in general be activated before they will react. It is interesting to notice three ways in which a molecule may gain energy and so become activated:

1. By collision with another swift-moving *material particle* (atom, molecule, ion).
2. By collision with a swift-moving *free electron.*
3. By collision with a photon of radiant energy.

If the molecule can be activated by the absorption of a very small amount of energy, namely, by a *low-energy quantum*, then a low frequency will be sufficient for activation, corresponding to the absorption of light in the infrared. If the activation energy is higher, a somewhat higher frequency will be required—light in the visible region, as in the photosynthesis of organic matter in the leaves of plants (p. 509). If the activation energy is still higher, ultraviolet light will be needed.

[1] It is probable that many substances may exist in several different activated states, each with its own particular reaction rate for any given reaction.

In being activated, a molecule may acquire a very high *kinetic energy* in comparison with an average molecule at that temperature; or it may have its *electronic energy* increased by having an electron raised to a higher energy level (§ 234). Its passage from an unactivated state to an activated state, with a higher content of energy, is represented as a passage from A to A', in Fig. 116.

325. Three Things that May Happen after Activation

After a molecule has been activated, any one of three things may happen:

1. The activated molecule may be *deactivated by collision with its neighbors*, handing on its surplus energy to them as increased kinetic energy, that is, as *heat*.

2. It may be *deactivated by release of a photon of radiant energy* (visible or invisible light) as a displaced electron reverts to a more stable lower energy level. This is *fluorescence* (p. 382).

3. It may enter into a *chemical transformation*, thereby suffering a decrease of energy to an energy level (B, Fig. 116) that is still *above* that of the original molecule, A; or to an energy level C that is *below* that of the original molecule. The former case is that of a reaction in which heat disappears and the latter case that of one in which heat is liberated.

326. Reactions Classified by Number of Molecules Concerned

An activated molecule sometimes *decomposes* or is *internally rearranged*, without colliding with any other molecule. This is termed a *unimolecular* reaction, since it is accomplished by a succession of *individual molecules*. Very few reactions of this type are known, and even these depend on previous activation of the molecules by collision with other molecules, with the walls of the containing vessel, or in other ways.

In other instances an activated molecule awaits collision with another molecule, then reacts with this by *direct union* or by *displacement* or *exchange*. This is termed a *bimolecular* reaction.

Occasionally *termolecular* reactions are encountered, in which a transformation is accomplished by the simultaneous collision of three different molecules. In mixtures of gases under ordinary pressures such termolecular collisions are hardly a thousandth part as frequent as bimolecular collisions.

In mentioning two different sorts of unimolecular reactions (*decomposition* and *rearrangement*) and three different sorts of bimolecular

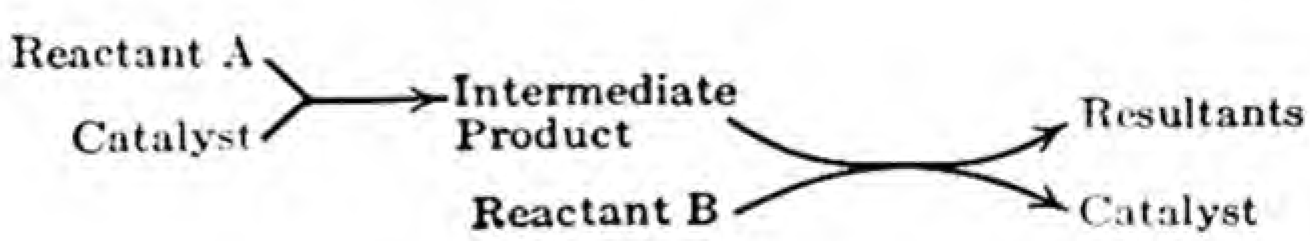
reactions (*direct union*, *displacement*, and *exchange*) we have accounted for the five chief types of chemical transformation, listed in § 28. A termolecular reaction may be any one of these five types. By the *mechanism* of a reaction we mean the manner of its accomplishment—whether unimolecular, bimolecular, or termolecular, with details of what happens in each case.

327. Two Different Kinds of Catalysts

What has just been said at once suggests that *catalysts act by activating molecules which would otherwise remain inactive.* We may then evidently have two different kinds of catalysts, hence two different kinds of catalysis:

1. In *homogeneous catalysis* the catalyst is dispersed in a uniform gaseous or liquid solution. In such instances the reaction rate is often (but not always) proportional to the concentration of the catalyst.

Molecules of the catalyst collide with and activate the reactant molecules and frequently combine with them to form an *intermediate product.* The molecules of the intermediate product then react with those of the other reactant to form definite resultants, regenerating the catalyst, which may be used again:



2. In *surface catalysis* the catalyst consists of a finely divided solid, such as platinum black [2] or highly porous charcoal. Catalysis takes place at the surface of the catalyst. We may visualize the surface of a crystalline catalyst as presenting an orderly array of atoms or ions at definite distances apart. When molecules of a reactant approach this surface they are attracted by the catalyst atoms in the surface. This attraction increases the number of reactant molecules in the immediate neighborhood of the surface, and so may lead to an increased reaction rate. More frequently, the reactant molecules enter into *temporary union* with the surface atoms of the catalyst, as if forming an intermediate compound, approaching a definite composition, in a film one molecule deep.

[2] Formed by reducing a dissolved platinum salt to metallic platinum, which precipitates as an extremely finely divided solid, and in consequence reflects light very poorly, and so appears black.

328. Details of What Happens in Surface Catalysis

The adhesion of the molecules of a gas or liquid to the surface atoms of a solid is called *adsorption*. This is really an example of *chemical union*, in which the adsorbed molecules share electrons with the underlying atoms of the solid. For example, when a layer of oxygen is adsorbed on a heated tungsten filament each tungsten atom shares one pair of electrons with an atom of oxygen and other pairs with neighboring atoms of tungsten. The result differs from an actual tungsten oxide only in the fact that all the tungsten atoms in the oxide, and not merely the surface atoms, are in chemical union with oxygen atoms, through shared electrons.

We can easily see that catalysis at a surface may consist of four successive steps:

1. Molecules of the *reactants*, diffusing through any intervening material, collide with the surface atoms of the catalyst and in favorable instances are adsorbed. The adsorbed molecules may be strained or distorted in being adsorbed, since they must accommodate themselves to the pattern formed by the surface atoms of the catalyst.

2. The adsorbed molecules, or the atoms that compose them, may migrate over the surface of the catalyst and so come into new positions with respect to one another, thus forming new molecules, those of the *reaction products*.

3. The new molecules thus formed part company with the underlying catalyst atoms, leaving these free to adsorb further molecules of the reactants.

4. The newly formed molecules of the reaction products ordinarily diffuse away from the catalytic surface into the interior of the surrounding gas or liquid. But in some instances they are deposited as a solid film, covering the surface of the catalyst and greatly restricting its action. Thus in the catalytic oxidation of sulfur dioxide to sulfur trioxide, in the commercial production of sulfuric acid (§ 315), the reaction is limited to the rate at which the reactant molecules (SO_2 and O_2) are able to diffuse through a layer of the solid reaction product, sulfur trioxide, deposited in a thin film on the surface of the catalyst!

In brief, *catalysis at a surface depends on the sharing of electrons between the adsorbed molecules and the underlying catalyst atoms, in a temporary union.* If the union is permanent the reaction ceases the moment the whole surface becomes covered with a layer of adsorbed material, one atom deep.

329. Effect of Impurities

We often find that a catalyst is "poisoned," in other words is *rendered inactive*, by the presence of very small amounts of certain impurities. Platinum black, for example, becomes inactive in the presence of traces of arsenic. We explain this as being due to the adsorption of the arsenic in permanent union with the surface atoms of the catalyst. Since the adsorbed layer needs to be only one atom deep it is not surprising that the merest trace of arsenic will stop the catalytic action of platinum black until the arsenic has in some manner been removed (for example, by being oxidized and dissolved by treatment with strong nitric acid).

Though traces of adsorbed impurities may render a solid catalyst inactive, nevertheless *the best catalysts are frequently those in which several different substances are intermingled in the catalytic surface.* Thus highly porous grades of charcoal are effective as catalysts in the oxidation of many organic compounds provided that they contain traces of iron, which are present in the charcoal as scattered atoms of metallic iron, serving as "active centers" for the oxidation. The merest trace of hydrogen cyanide, or of various other substances capable of reacting with iron, will render the catalyst inactive. We do not even need the slight trace of impurity that is needed to cover the whole surface of the charcoal one atom deep, but merely enough to cover the scattered atoms of metallic iron that form the active centers!

330. Current Research in Catalysis

Many research workers are actively engaged in studies of surface catalysis. These are revealing the reaction mechanism for many surface-catalyzed reactions of industrial importance, for example, those employed in the commercial production of ammonia (§ 366), nitric acid (§ 379), sulfur trioxide (§ 315), and methanol (§ 94). Better yet, general principles are being revealed that will permit chemists of the future to prepare more effective catalysts than any now known, for a multitude of reactions that can be accomplished only in the presence of a catalyst.

We know today that the best solid catalysts are not merely those in which the material is highly porous or finely divided, so as to give maximum surface. The space lattice of the solid should be riddled with cracks and fissures of less than microscopic size, thus giving a considerable number of catalyst atoms which are linked to their neighbors by only a single pair of electrons, and which in consequence

possess a maximum number of "free bonds" or unused electron pairs, for combining with the reactant molecules.

Furthermore a space lattice that is interrupted by foreign atoms is frequently a more effective catalyst than a pure material: witness the iron atoms serving as active centers in catalytic charcoal; or such mixtures as $Fe + Al_2O_3 + K_2O$, serving as a catalyst in the synthesis of ammonia; or $Cu + ZnO$, serving as a catalyst in the synthesis of methanol. *Very often a change in the nature of the catalyst will alter the identity of the resultants obtained from a given set of reactants.* Furthermore, many decomposition reactions are bimolecular in the absence of a catalyst and unimolecular in its presence.

331. Why Increased Temperature So Greatly Increases Reaction Rate

Now let us see if we can explain why a very slight increase in temperature often produces a startling increase in reaction rate. It is not sufficient to say that as the temperature is increased the molecules move more rapidly and collide more frequently. An increase of 10 per cent in the absolute temperature will make a 10 per cent increase in the *kinetic energy*, $\frac{1}{2}mv^2$, of an average-energy molecule, namely about a 5 per cent increase in the *velocity*, v (since $\sqrt{1.10} = 1.05$). This would make collisions about 5 per cent more frequent than before. But the reaction rate, at a 10 per cent higher temperature, is often 10 to 50 times its rate at the lower temperature—an increase of not merely 5 per cent, but 900 to 4900 per cent!

To clear up this mystery let us recall (§ 113) that *the molecules of a material, at any given temperature, do not all have the same velocity.* Only a few of them have sufficient velocity and hence sufficient energy to become activated and hence to react when they collide. But *a slight increase in the temperature will always very greatly increase the number of molecules having velocities above the "activating velocity," and hence will greatly increase the reaction rate.* It is as if all the students in a class in chemistry could be persuaded to put just a little more effort into their work. The class average might be increased only a few per cent; but we might find many passing with a grade above 90 who otherwise would have fallen just short of that standard.

332. How Reaction Rate Depends on Concentration

For a *unimolecular reaction* (one accomplished by the decomposition or internal rearrangement of separate *individual* molecules, § 326) the rate of the reaction under given conditions will depend on how

many molecules there are in each cubic centimeter of the reaction vessel. In other words, *reaction rate, under given conditions, in a unimolecular reaction, is proportional to the concentration of the substance being transformed.*

For a *bimolecular reaction* (one dependent on the collision of molecules in pairs) reaction rate, under given conditions, will depend on the frequency of such collisions. Collision frequency, in turn, will be proportional to the *concentration* of *each* of the two reacting substances, and therefore to *the product of their concentrations.* When hydrogen gas, for example, reacts with iodine vapor to form hydrogen iodide,

$$H_2 + I_2 \rightleftarrows 2HI$$

doubling the concentration of *either* of the two reactants will double the reaction rate. Doubling the concentration of *both* of them will multiply the reaction rate by 4. (Ex. 1, 2.)

For a *termolecular reaction* (only infrequently encountered) the reaction rate will similarly be proportional to *the product of three concentrations* (two or three of which will be identical whenever two or three of the molecules involved in the threefold collision happen to be of the same kind).

Consider, for example, the reaction

$$\underset{\text{Nitric oxide}}{2NO} + O_2 \rightarrow \underset{\text{Nitrogen dioxide}}{2NO_2}$$

If this is actually accomplished by the simultaneous collision of three particles (two of NO and one of O_2) the reaction rate will be proportional to the product of three concentrations: (conc. of NO) $\times$ (conc. of NO) $\times$ (conc. of O_2). Two of the colliding particles, hence two of the concentrations, are here *identical;* in other words the reaction rate is proportional to (conc. of NO)^2 $\times$ (conc. of O_2).

333. Reaction Order

Reactions are sometimes classed as *first-order, second-order,* or *third-order* according as they are found to proceed at a rate directly proportional to the concentration of some *one* reactant, or to the product of *two* or *three* concentrations (perhaps in part identical). *A first-order reaction may be a unimolecular reaction; or it may be a bimolecular reaction in which the concentration of one reactant varies, whereas the other is present in so large an excess that its concentration remains practically constant* Similarly for second-order and third-order reactions. (Ex. 3.)

A reaction of *zero order* is one whose rate is independent of the concentrations of the reactants. A reaction whose rate is determined by the supply of *radiant energy*, or *a surface-catalyzed reaction, with the surface of the catalyst fully occupied, are examples.*[3]

334. Monatomic Particles

Monatomic hydrogen, oxygen, or chlorine may readily be prepared by the action of an electric discharge through these gases under low pressure, thus imparting extra energy to the molecules, in collisions with swift-moving free electrons:

$$Cl_2 + \text{Energy} \rightarrow 2Cl'$$

(Note the use of an accent mark or a star to represent activation.) The free atoms thus produced are much more reactive than ordinary molecules of the same elements. Monatomic hydrogen (§ 95) reacts with numerous metals, even at liquid-air temperatures, to give *hydrides*. It will also react with solid sulfur and iodine, forming hydrogen sulfide and hydrogen iodide.

A mixture of hydrogen and oxygen may be caused to explode by the introduction of a few particles of monatomic hydrogen. A trace of monatomic chlorine will similarly bring about the union of hydrogen and chlorine to form hydrogen chloride. This is evidence that these reactions are actually accomplished in a series of successive steps, in at least the first of which the activated particles are monatomic. We must not conclude, however, that the activated particles are monatomic in all reactions. *The decomposition of a molecule into atoms takes place only when the energy of vibration of the atoms within the molecule, as a result of energy gained in activation, is sufficient to break the bonds between the atoms.*

One might expect the monatomic particles, obtained by decomposing diatomic particles, to recombine immediately:

$$2Cl' \rightarrow Cl_2 + \text{Energy}$$

Such a reaction apparently cannot take place in the absence of a third body to accept the energy set free. In other words, *the direct union of two monatomic particles ordinarily does not occur except in a triple collision involving a third particle, or at the surface of a solid.*

[3] When the reactants are present in such slight concentration that very little of the catalyst surface is occupied at any given moment the reaction is of the first order or some higher order.

335. Chain Reactions

Many reactions are known in which *the activation of a single molecule may cause a series of successive reactions to take place*, until a large number of molecules have been transformed. Thus, when hydrogen gas is mixed with chlorine in the presence of a little moisture, the introduction of a trace of sodium vapor or monatomic hydrogen, or the incidence of a very slight amount of radiant energy of proper wavelength, is sufficient to activate a few molecules of chlorine:

$$Na + Cl_2 \rightarrow NaCl + Cl'$$

or

$$Cl_2 + \underset{\text{Radiant energy}}{h\nu} \rightarrow 2Cl'$$

Each particle of monatomic chlorine thus produced reacts with a molecule of hydrogen, to produce a molecule of hydrogen chloride and a particle of activated hydrogen:

$$Cl' + H_2 \rightarrow HCl + H'$$

The activated hydrogen, in its turn, may react with a molecule of chlorine, producing still another molecule of hydrogen chloride and a particle of activated chlorine:

$$H' + Cl_2 \rightarrow HCl + Cl'$$

This process can continue indefinitely, forming a "chain" of reactions, or *chain reaction*, in which the active particles are alternately Cl′ and H′. In each successive stage or "link" of the chain a particle is produced that is in an activated condition and is able to enter into another reaction.

Chain reactions in general resemble the one just described in being very sensitive to *traces of added impurities*. These may greatly increase the reaction rate by activating new molecules, thus beginning new chains, or may greatly decrease it by deactivating the reaction products, thus bringing the chains to an end before they have transformed any considerable amount of material.

When chain reactions are carried on in capillary tubes or in vessels loosely filled with glass wool the reaction rate is very greatly decreased by prompt deactivation of reaction products by collision with the walls. We thus account for the fact that *the propagation of a flame or an explosion through a tube is often prevented by a loose plug of cotton or glass wool.* (Ex. 4, 5.)

A reaction otherwise insensitive to light is often made light-sensitive by the presence of certain impurities. The impurities are said to *photosensitize* the reaction. For example, a mixture of hydrogen and oxygen gases is insensitive to light unless a slight trace of ammonia is present. In the presence of this, ultraviolet light causes an explosion. An explanation is found in the fact that ammonia is decomposed by ultraviolet light:

$$NH_3 + \underset{\text{Radiant energy}}{h\nu} \rightarrow NH'_3 \rightarrow NH'_2 + H'$$

The activated hydrogen thus produced initiates a chain of reactions, in which hydrogen and oxygen combine to form water. That the reaction is really produced in the manner indicated is seen in the fact that a trace of monatomic hydrogen or chlorine, introduced from an outside source, will initiate an explosion quite as effectively as momentary exposure to ultraviolet light in the presence of a trace of ammonia. (Ex. 6.)

For a review of this chapter see Exercises 7–25.

Technical Words

Enzyme—an organic catalyst produced by a living organism.

Reaction rate, p. 370. **Particle concentration,** p. 371.

Unimolecular, bimolecular, termolecular reaction, pp. 378, 379.

Homogeneous catalysis, p. 375. **Surface catalysis,** p. 375.

Adsorption—the adhesion of the molecules of one material to the surface of another.

Absorption—the passage of one material into the interior of another, either by dissolving in it or by penetrating pores or crevices.

First-order, second-order, third-order reaction, p. 379.

Zero-order reaction, p. 380.

Steady state—a condition of balance, in which each intermediate product, in a reaction taking place in successive stages, is produced at the same rate as that at which it disappears. The final product is then produced at a rate proportional to the product of the concentrations of the substances concerned in the first stage of the reaction.

Activated—possessed of a suitable structure or a sufficient supply of energy to take part in a specified reaction.

Chain reaction—a reaction that is accomplished in a series of successive stages, each of which yields one or more activated particles, to react in the next following stage.

Photochemical reaction—a reaction induced or greatly accelerated by light.

Photosensitization—an effect of traces of certain impurities, in causing certain reactions to be induced or accelerated when the material is exposed to light. The

molecules of the photosensitizing impurity are activated by collision with photons of the radiant energy, then enter into a reaction or a series of reactions.

Fluorescence—the absorption of radiant energy by a substance and its instantaneous re-emission as radiant energy (usually of lower frequency).

Secondary reaction or **side reaction**—a reaction in which specified reactants are transformed into other products than those produced in a concurrent *primary reaction*. The *yield* of the primary reaction is thereby diminished.

Yield—the quantity of a desired product obtained in a given reaction, in comparison with that which would have been obtained if the reaction (1) had been complete, (2) had been unaccompanied by side reactions, and (3) had resulted in complete recovery of the product. The weight or volume of product, calculated from the balanced chemical equation, represents a yield of 100 per cent.

Exercises

1. How will the rate of union of hydrogen and iodine to form hydrogen iodide be affected by doubling the concentration of the hydrogen, but reducing the concentration of the iodine to one-fourth its former value?

2. A mixture contains 3 moles of hydrogen and 2 moles of iodine vapor. How will the rate of union of the two substances, in the beginning, compare with the rate after half of the iodine has disappeared by combining with an equal number of moles of hydrogen?

3. When the class of organic compounds known as esters (§ 464) react with water the products are an alcohol and an organic acid. Explain why this is a first-order reaction, whenever the water is in very great excess.

4. A mixture of hydrogen and oxygen may be caused to explode by introducing a little platinum black (finely divided metallic platinum). Write equations for successive steps in a chain reaction which may possibly occur, assuming that the platinum activates the hydrogen.

5. When a mixture of gasoline vapor and air, in an automobile engine, burns too rapidly, the result is audible as "knocking." Explain why many foreign substances, including lead tetraethyl, when introduced into gasoline, diminish or prevent knocking.

6. The direct union of hydrogen and oxygen to form hydrogen peroxide is photosensitized by mercury vapor. Give an equation for the reaction by which the mercury becomes activated and in turn activates the hydrogen.

7. What are the units in which reaction rate is commonly expressed?

8. What is meant by particle concentration? What is the effect of doubled particle concentration on the rate of a first-order, second-order, and third-order reaction, respectively?

9. What is meant by photosynthesis?

10. What is meant by activation? Indicate at least three different ways in which a molecule may become activated.

11. What are the three chief ways in which an activated molecule may lose its store of extra energy?

12. What is meant by fluorescence?

13. What is the difference between a unimolecular reaction and a first-order reaction?

14. What is meant by the mechanism of a reaction?

15. What are the two chief classes of catalysts?

16. What is meant by adsorption?

17. Indicate four successive stages that may be involved in a surface-catalyzed reaction.

18. Explain why surface catalysts are frequently rendered inactive by the presence of traces of impurities.

19. Explain why a slight increase in temperatures very frequently produces a very great increase in reaction rate.

20. In the direct union of nitric oxide with oxygen to form nitrogen dioxide (§ 332), how many molecules of nitric oxide are transformed for each molecule of oxygen? If we start with a mixture of 5 moles of nitric oxide and 2 of oxygen, how many moles of nitric oxide will still remain when half of the oxygen originally present has been transformed? How will the reaction rate at this moment compare with that in the beginning? *Ans.*, 9/50.

21. Explain how monatomic hydrogen, oxygen, or chlorine may be prepared.

22. What is meant by a chain reaction? Give an example of a chain reaction initiated by light, with equations to show what really happens.

23. State Einstein's Photochemical Law. Explain why the amount of material transformed by a single quantum of radiant energy may nevertheless vary from zero to some very large number of molecules.

24. What determines the energy that a molecule may gain in collision with a photon?

25. What is meant by photosensitization? Give an example.

Chapter 25

CHEMICAL EQUILIBRIUM

336. Balanced Reaction Rates

In previous chapters we have had many instances of chemical reactions that are *reversible*. In every such instance the two oppositely directed reactions finally come to proceed at equal rates, each undoing the work of the other. We then have a condition of *chemical equilibrium:*

Formation of ozone:	$3O_2 \rightleftharpoons 2O_3$
Ionization of a slightly active acid:	$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$
Reaction of chlorine with water:	$Cl_2 + H_2O \rightleftharpoons HCl + HClO$

By the use of heavy arrows we have indicated that the concentration of each substance to the left of the double arrow, when equilibrium is reached, is greater than the concentration of any substance to the right, in each of the three reactions here considered. The equilibrium mixture, under ordinary conditions, is sure to contain far more oxygen than ozone, far more acetic acid molecules than ions, far more chlorine than hypochlorous acid. In brief, *equilibrium represents an equality of opposing reaction rates, not an equality of concentrations.* A man is in financial equilibrium when his income equals his expenditures; but his actual balance in the bank, at that moment, may or may not exceed his debts. We can only be sure that his net rate of progress toward wealth or toward bankruptcy has, at least for the moment, been reduced to zero.

337. Approach toward Equilibrium

It is interesting to follow the details of an *approach toward equilibrium.* Let us mix two reactants, A and B, which react reversibly to form C and D:

$$A + B \underset{(b)}{\overset{(a)}{\rightleftharpoons}} C + D$$

At the first moment only the forward reaction (*a*) can take place, since C and D are absent. The rate of this forward reaction is proportional to the product of the concentrations of A and B (§ 332). But since A and B are steadily being transformed, the concentration of each, hence the rate of the forward reaction, steadily *decreases*, as in Fig. 117.

The reverse reaction (*b*), on the contrary, uses reactants, C and D, whose concentration is steadily increased by the predominating for-

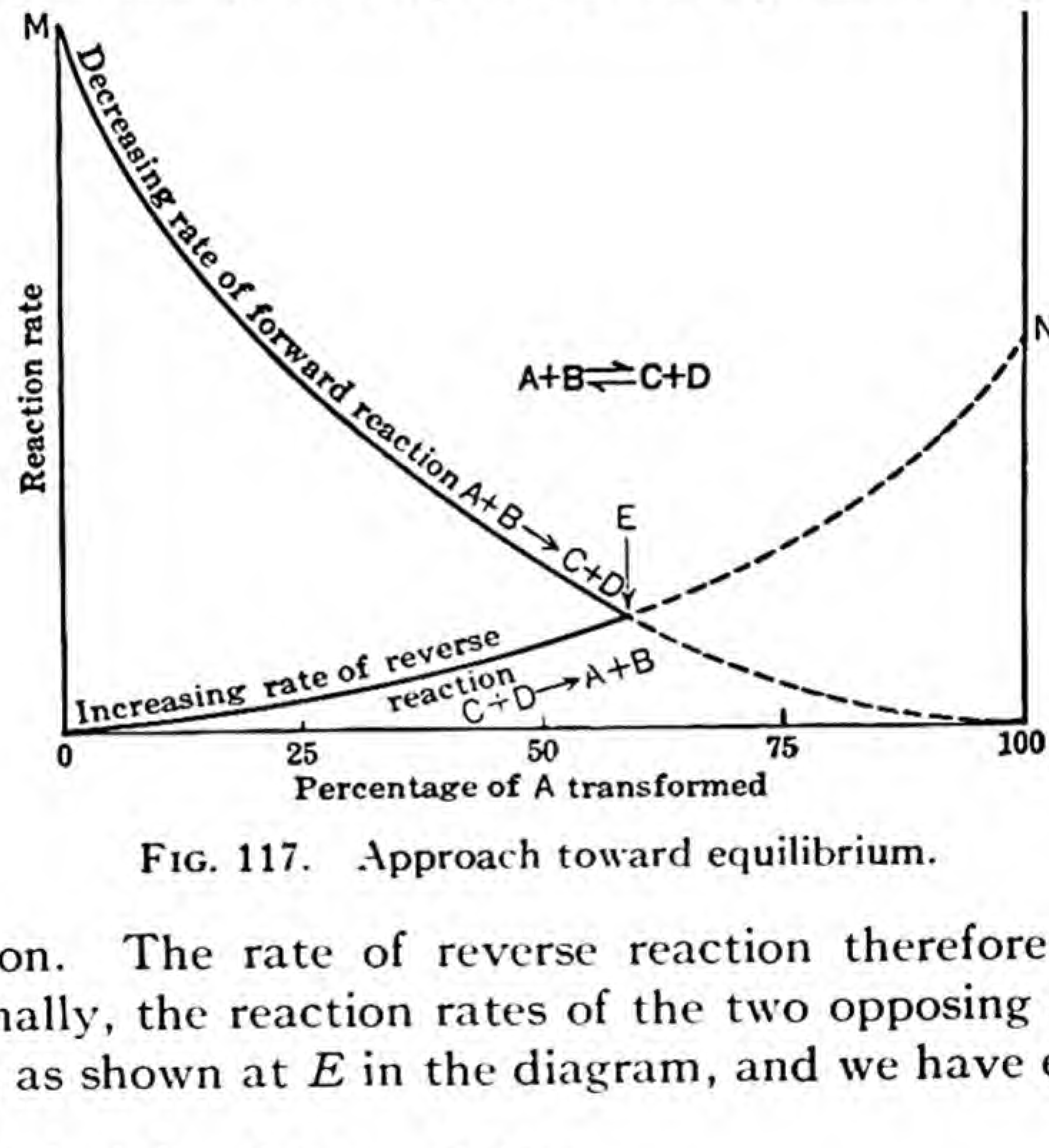


FIG. 117. Approach toward equilibrium.

ward reaction. The rate of reverse reaction therefore steadily *increases*. Finally, the reaction rates of the two opposing reactions become equal, as shown at *E* in the diagram, and we have equilibrium.

338. The Principle of Mass Action

In the reversible reaction

$$A + B \rightleftharpoons C + D$$

an increase in the concentration of A will proportionately increase the speed of the forward reaction without immediately affecting the speed of the reverse reaction. Thus when equilibrium is reached *a larger proportion* of B will have been transformed than before.

Similarly, by increasing the concentration of B we may increase the speed of the forward reaction without immediately affecting that of the reverse reaction, and so at equilibrium will have transformed a larger proportion of A than we otherwise would.

The same result might have been obtained in another way, namely by decreasing the concentration of either of the two resultants, C or D, perhaps by having them combine with something else, to form a slightly soluble product, separating as a precipitate. By thus decreasing the concentration of C or D we would decrease the speed of the reverse reaction without immediately affecting that of the forward reaction. In consequence, the proportion of A or B transformed at equilibrium would be increased.

To summarize: *The transformation of any chosen reactant in a reversible chemical reaction may be made more nearly complete by increasing the concentration of any other reactant or by decreasing the concentration* of any resultant. This is called the *Principle of Mass Action.* Nevertheless, observe that it is not mass that counts but *mass in unit volume*, in other words, *concentration.*

The principle just given is sometimes expressed by saying that by increasing the concentration of either of the reactants or by reducing the concentration of either of the resultants we "shift the equilibrium toward the right." This is chemical jargon, meaning that we have made the left-to-right reaction more nearly complete.

339. Some Applications

As an application of the Principle of Mass Action consider the reversible union of sulfur dioxide with oxygen:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

This is a step in the important contact process for the preparation of sulfuric acid (§ 315). The object is to make the most complete conversion possible of the sulfur dioxide into sulfur trioxide. The Principle of Mass Action tells us that this may be accomplished by the use of an *excess of oxygen*, in other words, more than the 1 volume or 1 mole of oxygen that is indicated by the equation for every 2 volumes or 2 moles of sulfur dioxide.

As an application of the Law of Mass Action to a reaction involving ions consider the oxidation of an arsenite to an arsenate. The balanced half equation (§ 262) is:

$$AsO_2^- + 2H_2O \rightleftharpoons AsO_4^{---} + 4H^+ + 2e$$

We can make the left-to-right reaction more nearly complete than it otherwise would be by decreasing the concentration of the resultant, H^+, that is, by carrying out the reaction in a neutral or alkaline solution, instead of in an acid solution. (Ex. 1, 2.)

The Principle of Mass Action tells us that a reaction always becomes very nearly complete whenever one of the products of the reaction (1) is carried away as a gas or (2) settles out as a precipitate (thus being practically removed from the field of reactions).

340. The Equilibrium Constant

The Principle of Mass Action enables us to predict whether a reversible reaction will be made more or less nearly complete by a change in the concentrations of the *equilibrants*. But if we inquire how much more nearly or less nearly complete it will be, as a result of these changes, we must resort to a calculation which may seem a bit complicated, though simple in principle. Consider the reaction:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + \mathrm{D}$$

We here assume that *one* molecule of A reacts for each molecule of B. Let us represent the reaction rate of the forward reaction by k_1, when both the reactants A and B are present in *unit concentration* (namely, 1 mole of each in 1 liter). Now let more molecules of A and B be introduced from some outside source, so that the concentrations of A and B become respectively [A] and [B]. This will proportionately increase the reaction rate, which will now be $k_1 \times [\mathrm{A}] \times [\mathrm{B}]$.

Similarly for the reverse reaction. Let us represent its reaction rate by k_2, when both the reactants C and D are present in *unit concentration*. If we increase the concentrations of these two reactants to [C] and [D] respectively, this will proportionately increase the reaction rate, which will now be $k_2 \times [\mathrm{C}] \times [\mathrm{D}]$.

At equilibrium the two opposing reaction rates are equal, namely

$$k_1 \times [\mathrm{A}] \times [\mathrm{B}] = k_2 \times [\mathrm{C}] \times [\mathrm{D}]$$

Let us represent k_1/k_2 by the symbol K_c. Then from the equation just given we find

$$K_c = \frac{k_1}{k_2} = \frac{[\mathrm{C}] \times [\mathrm{D}]}{[\mathrm{A}] \times [\mathrm{B}]}$$

The quantities k_1 and k_2 are called *specific reaction rates.* They show the rates at which the forward and reverse reactions proceed at some chosen temperature, when all the reactants are present in *unit concentration.* The ratio of the two specific reaction rates, $K_c = k_1/k_2$, is called the *equilibrium constant.* This may always be found, when-

ever we know the concentrations of the reacting substances *at equilibrium*, by taking the ratio

$$\frac{[C] \times [D]}{[A] \times [B]}, \text{ namely } \frac{\text{Product of concentrations of resultants}}{\text{Product of concentrations of reactants}},$$

at the given temperature, for any reversible reaction of the simple type just considered. (Ex. 3.)

Remember that the numerical value of an equilibrium constant is determined by *the nature of the reaction* and by the *temperature*. It does not depend on which reactant is present in excess, nor is it perceptibly altered by ordinary changes in pressure.

In calculating an equilibrium constant it is customary to consider a pure solvent or a solid as being present in unit concentration. In dilute aqueous solutions water is present in nearly the same concentration as in pure water, is therefore present in unit concentration, and so may be omitted from the expression for the equilibrium constant.

341. Large and Small Values for the Equilibrium Constant

When the equilibrium constant, $K_c = k_1/k_2$, is *large* (decidedly over 1) this means that the forward reaction, under comparable conditions, proceeds much faster than the reverse reaction—a greater fraction of collisions resulting in reaction. The *forward reaction* therefore drives forward until its products, C and D, have accumulated to high concentrations while A and B have meanwhile nearly completely disappeared. The high concentrations of C and D then enable the *reverse reaction* to overcome the handicap of low specific reaction rate. The forward and reverse reactions henceforth proceed at equal rates, and we have equilibrium.

On the contrary, an equilibrium constant decidedly less than 1 indicates that the forward reaction, under comparable conditions, proceeds much less rapidly than the reverse reaction, hence A and B accumulate while C and D dwindle. Finally the concentrations of A and B get so high that the forward reaction is able to proceed at the same speed as the reverse reaction, in spite of the handicap of a low specific reaction rate.

In any event the ratio $\frac{[C] \times [D]}{[A] \times [B]}$ at equilibrium will be a measure of the ability of the forward reaction, *under given conditions*, to produce and accumulate C and D, in comparison with the ability of the reverse reaction to produce and accumulate A and B. It must therefore be

the same as the ratio of the specific reaction rates, k_1/k_2, as already proved.

342. The Equilibrium Constant for a Reaction in Stages

A reaction may be known to take place in several successive steps, by way of intermediate products. Then when equilibrium is reached we shall have a separate equilibrium constant for each step. Thus the reaction

$$A + 3B \rightleftharpoons AB_3$$

may be known to proceed in three separate steps:

$A+B \rightleftharpoons AB$, followed by $AB+B \rightleftharpoons AB_2$, followed by $AB_2+B \rightleftharpoons AB_3$

The equilibrium constants will then be:

$$K_1 = \frac{[AB]}{[A] \times [B]} \qquad K_2 = \frac{[AB_2]}{[AB] \times [B]} \qquad K_3 = \frac{[AB_3]}{[AB_2] \times [B]}$$

Now take the product of these equilibrium constants. The concentrations of the intermediate products, AB and AB_2, cancel out and we have

$$K_c = K_1 \cdot K_2 \cdot K_3 = \frac{[AB_3]}{[A] \times [B]^3}$$

This is precisely the result that we should have obtained for the equilibrium constant if we had considered our reaction, $A + 3B \rightleftharpoons AB_3$, as taking place in a *single step*, by the simultaneous collision and direct union of four molecules. In other words, since concentrations of the intermediate products cancel out, *we need not concern ourselves about the intermediate steps of any reaction, but may write its equilibrium constant as if it were accomplished in a single step, as indicated by the chemical equation, however complicated.*

To summarize: The equilibrium constant, K_c, for any reaction, is

(*Product of appropriate powers of the concentrations of resultants*) ÷
(*Product of appropriate powers of the concentrations of reactants*)

By appropriate powers of the concentration we mean that each concentration must be raised to a power that is indicated by the number of molecules of that substance appearing in the balanced equation. We must *square* the concentration of any substance for which *two* molecules appear in the balanced chemical equation, *cube* the concentration of any substance for which *three* molecules appear, etc. (Ex. 4.)

343. Equilibrium Constant in Terms of Partial Pressures

When the reactants in a chemical reaction are all gases, the equilibrium constant K_c is usually replaced by another constant, K_p, which is defined as:

(Product of appropriate powers of the partial pressures of resultants) ÷ *(Product of appropriate powers of the partial pressures of reactants)*

For example, in the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

when the three gases were in equilibrium under high pressure at a certain temperature, their partial pressures were found to be 100, 300, and 20 atmospheres, for nitrogen, hydrogen, and ammonia, respectively. Then K_p, at that temperature, was

$$\frac{20^2}{100 \times 300^3} = 1.5 \times 10^{-7}$$

(Check this.)

The partial pressure of vapor in equilibrium with a solid or a nearly pure liquid solvent is arbitrarily taken as unity, and so disappears from the expression for K_p.

344. Making Use of the Equilibrium Constant

The equilibrium constant for any given reaction has *a definite value for each temperature* and *does not vary with the proportions in which the reacting materials are brought together* or with ordinary changes in *pressure.* Furthermore, the presence or absence of catalysts has no effect on the equilibrium constant. This must be true since a catalyst acts by producing an intermediate product in the midst of a homogeneous solution or at the surface of a solid; and we have already seen that the concentrations of the intermediate products cancel out of our final expression for the equilibrium constant.

The equilibrium constant for any given reaction does vary with the temperature, sometimes becoming greater and sometimes less as the temperature is raised (§ 346).

Now for an example of the use of the equilibrium constant in predicting how nearly complete a reaction will be when the reactants are brought together in chosen proportions:

If 0.32 mole of hydrogen gas and 0.32 mole of iodine vapor are brought together in a volume of 5 liters at a temperature at which K_c = 50, how

many moles of hydrogen iodide will be produced and how many moles of each of the reactants will remain untransformed?

Set down everything in an orderly way:

	H_2	+	I_2	$\rightleftharpoons$ 2HI	$V = 5$ liters
Moles at start........................	0.32		0.32	0	
Moles transformed (−) or produced (+)	$-x$		$-x$	$2x$	
Moles at equilibrium..................	$0.32 - x$		$0.32 - x$	$2x$	

We have assumed that x moles of hydrogen will be transformed. The chemical equation shows that an equal number of iodine molecules will be transformed, and that twice that many molecules of hydrogen iodide will be produced. This explains the entries $-x$, $-x$, and $+2x$ for moles transformed or produced. Divide the moles at equilibrium by 5 (the total volume, in liters) to find the concentrations in moles per liter. For the equilibrium constant we then have

$$K_c = \frac{(2x/5)^2}{\left(\frac{0.32 - x}{5}\right)^2} = 50$$

If we solve this as a quadratic equation in x we find $x = 0.25$, very nearly. Thus the moles at equilibrium will be $0.32 - 0.25 = 0.07$ for the hydrogen, the same for the iodine, and $2 \times 0.25 = 0.50$ for the hydrogen iodide. Check by substituting in the equation, to see what value is obtained for K_c.

In the expression just given for the equilibrium constant it will be noticed that the volume, 5 liters, cancels out. We would have obtained the same concentrations of the equilibrants at equilibrium whatever the total volume of the mixture. The volume will always cancel out whenever the same number of molecules appear on the left-hand side of the chemical equation as on the right-hand side. Otherwise expressed, *the reaction volume has no effect on the final condition of equilibrium if the chemical transformation produces no alteration in the total number of molecules.* (Ex. 5, 6.)

345. Another Example

In problems dealing with equilibrium it is not really necessary to resort to algebra to find the final value of x. If algebra is used we often encounter equations involving the cube of x or even higher powers. We may avoid these difficulties by making several successive guesses at the progress that the reaction must make to obtain equilibrium.

For example, when phosphorus pentachloride, PCl_5, is heated it is vaporized and in part reversibly decomposed (dissociated) as shown by the equation below, forming phosphorus trichloride, PCl_3, and free chlorine. *How many moles of free chlorine will be produced when 0.1 mole of phosphorus pentachloride is vaporized in a total volume of 2 liters, at a temperature at which the equilibrium constant, K_c, is known to be 0.04?*

Again set down all the data in an orderly way:

	PCl_5 $\rightleftharpoons$	PCl_3 +	Cl_2	V = 2 liters
Moles at start	0.1	0	0	
Moles transformed (−) or produced (+)	$-x$	$+x$	$+x$	
Moles at equilibrium	$0.1 - x$	x	x	

Divide the moles at equilibrium by 2 (the total volume, in liters) to find the concentrations in moles per liter. Then,

$$K_c = \frac{(x/2)^2}{\left(\dfrac{0.1 - x}{2}\right)} = 0.04$$

Here the reaction produces a change in the total number of molecules, hence the volume of the reaction mixture will not cancel out. Instead of solving for x in the expression just given for the equilibrium constant, let us try to guess its value. Since K_c is very much less than 1 we may conclude that the left-to-right reaction is much *slower* than the opposing reaction, under comparable conditions, hence the reaction cannot be very nearly complete. Let us guess that *half* the original phosphorus pentachloride is transformed, in other words that $x = 0.05$ mole in the expression above. We then find $K_c = 0.025$, which is *not quite large enough.* So let us assume a somewhat larger value for x, namely 0.06. We then find that $K_c = 0.045$.

The true value, $K_c = 0.04$, lies between the values 0.025 and 0.045, obtained in our two trials, and is just three fourths of the way from the first to the second of these values. Then traversing three fourths of the distance from our first guess, $x = 0.05$, to our second, $x = 0.06$, we obtain $x = 0.058$ for the true number of moles of chlorine produced. The *concentration* of chlorine, in moles per liter, will be half this value, since the reaction was carried out in a total volume of 2 liters. (Ex. 7.)

346. Effect of Temperature on Equilibrium

When we remarked that the equilibrium constant is unaffected by altering the proportions in which the reactants are intermingled or by

altering the pressure we were really assuming that *some definite proportion of all collisions between molecules results in reaction.* This is true only if the temperature remains unaltered.

Even a slight increase in temperature gives a much higher proportion of collisions in which the molecules receive enough energy to be activated (§ 331). So even a slight increase of temperature results in a higher reaction rate for *whichever* of the two opposing reactions is dependent for its supply of energy on collisions with unusually swift-moving neighboring molecules, namely for *whichever* of the two opposing reactions results in the disappearance of heat. The other reaction, in which heat is set free, is one in which the reactant molecules possess a surplus of energy, which they can transfer to their neighbors, and in consequence are not to the same degree dependent for activation on collision with swift-moving neighbors.

In brief, when a mixture of substances is in chemical equilibrium, an increase of temperature always accelerates the reaction in which heat disappears more than it does the reverse reaction. Consequently, an increase in temperature always renders a reversible reaction in which heat disappears *more nearly complete*, and the opposing reaction, in which heat is set free, *less nearly complete*. This is sometimes called *Van't Hoff's Principle.*

For example, the union of sulfur dioxide and oxygen, to produce sulfur trioxide

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

is one in which the *left-to-right* reaction liberates heat. In consequence, it is most nearly complete at *low temperatures.*

Too low a temperature, however, would certainly make the reaction too slow. We compromise, by using as low a temperature as will still give us a reasonable reaction rate, in the presence of the best catalyst we can find. Whenever a catalyst is found useful we can be very sure (1) that the reaction is reversible, liberating heat and so being most nearly complete at low temperatures; or (2) that it is a reaction which for some reason cannot well be carried out at high temperatures.

Textbooks of physical chemistry give an equation that permits one to calculate how much the equilibrium constant will be altered and accordingly just what changes in the equilibrium concentrations will be induced by any given change in temperature. (Ex. 8.)

347. The Principle of Le Chatelier

The Principle of Van't Hoff is really a consequence of a much broader principle. Let us recall that a system is in equilibrium when all

forces and processes within the system are balanced by opposing forces and processes. If we now alter any of the conditions that determine the *energy* of the system (for example the pressure or the temperature) this will often bring new forces into action within the system and disturb the equilibrium previously existing.

But whenever a force acts it always does so in such a manner as to relieve the force, namely to diminish potential energy (§ 67), and so bring the system back toward its original condition. Briefly expressed, *a system in equilibrium will remain indefinitely in equilibrium unless surrounding conditions are changed; a change then takes place within the system that tends to restore the original conditions.* This is the *Principle of Le Chatelier.*

Let us apply this principle to the effect of increased pressure on the synthesis of ammonia:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 26.74 \text{ kilocalories } (400°\text{C}, 100 \text{ atm})$$

Since 4 molecules produce 2 molecules in the left-to-right reaction, this results in a decrease in the total number of molecules in the system, and hence in a decrease in the total pressure that the mixed gases exert. According to Le Chatelier an increase in the pressure on the reaction mixture will cause the change to take place that will *decrease* the pressure, toward its original value. The result of an increase in pressure must therefore be to make the left-to-right reaction more nearly complete and the opposing reaction less nearly complete. We sometimes express this by saying that the increase in pressure has "favored" the left-to-right reaction. (Ex. 9.)

Let us now check the effect of increased temperature on this reaction. According to Le Chatelier increased temperature must favor the reaction that tends to result in a *decrease* in temperature, heat disappearing. In other words, the right-to-left reaction is made more nearly complete by an increase of temperature and the opposing reaction less nearly complete. This checks our previous conclusion. (Ex. 10.)

The Principle of Le Chatelier applies only to systems that are already in equilibrium at the time the change in conditions takes place. Hydrogen and oxygen gases will remain in contact with each other indefinitely, at room temperature, without reacting; but if the temperature is raised, by passing an electric spark, an explosion takes place, forming water and liberating heat. It appears at first as if an increase in temperature had favored a reaction liberating heat and resulting in a further increase in temperature, in violation of Le Chatelier's Principle

The trouble is that hydrogen and oxygen are not really in equilibrium with water vapor at room temperature, and Le Chatelier's Principle cannot apply. (Ex. 11.)

It is easy to distinguish true equilibrium from a reaction that is proceeding with extreme slowness or perhaps has ceased entirely for lack of a sufficient temperature or other means to activate the molecules. *In true equilibrium a small decrease of temperature will always reverse the effect of a small increase of temperature;* but if hydrogen and oxygen are made to combine by raising the temperature, we find that lowering the temperature does not cause the water to decompose again into hydrogen and oxygen. This is therefore not an example of true equilibrium.

For a review of this chapter see Exercises 12–24.

Technical Words

Equilibrium, p. 385. **Concentration,** p. 387.

Specific reaction rate—the rate at which a reaction proceeds at some chosen temperature, when each reactant is present in unit concentration.

Equilibrium constant—a number that is characteristic of a specified chemical reaction *at any specified temperature.* It is found by taking the product of appropriate powers (p. 390) of the concentrations of the *resultants* in an equilibrium mixture, then dividing this result by the product of appropriate powers of the concentrations of the *reactants.*

Equilibrants—the substances concerned in any equilibrium.

Exercises

1. Explain how the preparation of a hypochlorite according to the method in § 204 illustrates the Principle of Mass Action.

2. When electric sparks are passed through a mixture of nitrogen and hydrogen the union of the two gases to form ammonia is always far from complete; but if sulfuric acid is present the reaction finally becomes complete. Explain.

3. Write an expression for the equilibrium constant in the reaction

$$A + B \rightleftharpoons C + D + E$$

Explain what is meant by each of the symbols in brackets.

4. Write an expression for the equilibrium constant of the reaction in which nitric oxide combines with oxygen to form nitrogen dioxide (§ 332).

5. Following the model in § 344, consider the reaction

$$H_2 + CO_2 \rightleftharpoons CO + H_2O$$

In the beginning there were present 5 moles of H_2, 2 moles of CO_2, 1 mole of CO, and 0 mole of H_2O. What will be the concentration of each of the four reactants

when half of the CO_2 has been transformed? If the mixture is then in equilibrium what is the numerical value of the equilibrium constant?

6. Explain why we did not need to know the volume of the reaction mixture in finding the equilibrium constant in Exercise 5.

7. Following the model in § 344, calculate the equilibrium constant if 1 mole of PCl_5, contained in a total volume of 5 liters, is 60 per cent dissociated at a given temperature.

8. Reword Van't Hoff's Principle, using the terms exothermic reaction and endothermic reaction (§ 82).

9. Write equations for the following reactions and indicate which of them are made more nearly complete and which less nearly complete by an increase in pressure:

Union of nitric oxide, NO, with oxygen to form nitrogen dioxide, NO_2.
Direct union of sulfur dioxide and oxygen to form sulfur trioxide.
Union of hydrogen and iodine to form hydrogen iodide.
Dissociation of ozone to form ordinary oxygen.

10. The dissociation of the molecule of a stable substance results in the disappearance of heat, since energy must be expended in overcoming the forces that link atoms together within the molecule. What may we conclude with regard to the effect of increased temperature on the degree of dissociation of a stable substance?

11. Ice and a few other substances occupy a smaller volume in the liquid state than in the solid state, hence melting tends to relieve any pressure that may be applied to the solid. Determine whether an increase in pressure, with such a substance, will favor or hinder the melting process, and so *lower* or *raise* the melting point.

12. Explain why the reaction rate of the forward reaction continuously decreases, whereas that of the reverse reaction continuously increases, as equilibrium is approached.

13. State the Principle of Mass Action. Show how it applies in the production of ammonia by the direct union of nitrogen and hydrogen.

14. If a reversible reaction produces an acid, what method may be used for making the reaction more nearly complete than it otherwise would be? What method for making it less nearly complete?

15. Write equations to show that hypochlorous acid, in solution in water, is but slightly ionized, whereas perchloric acid is almost completely ionized.

Suggest a way to insure the formation of a larger proportion of hypochlorite ion, from hypochlorous acid.

16. What name is given to the substances that appear as reactants and resultants in a reaction that has reached equilibrium?

17. What is meant by specific reaction rate?

18. Show how one may calculate the equilibrium constant for the synthesis of ammonia, if the concentrations of the three equilibrants are known at some definite temperature.

19. Indicate two variations of conditions that do not alter the value of the equilibrium constant, and one that does alter it.

20. Explain what practical interest is served in knowing the numerical value of the equilibrium constant of a reaction at some temperature.

21. When does the volume in which a reaction takes place have no effect on the equilibrium constant or on the degree of completeness of the reaction (§ 344)?

22. State the Principle of Van't Hoff, and show how it applies to exothermic and endothermic reactions, respectively.

23. State the Principle of Le Chatelier. Apply it to the effect of pressure on a reaction in which the total number of molecules respectively decreases, remains constant, or increases as a result of the reaction.

24. Explain how one may determine whether a mixture of substances has actually reached a condition of equilibrium.

Chapter 26

THE ATMOSPHERE

As a preliminary to the study of the chemistry of nitrogen it seems well to devote a chapter to the atmosphere, in which elementary nitrogen, owing to its chemical inertness, serves chiefly to dilute oxygen and so to restrain the activity of that element, in respiration, combustion, rusting, and decay, to about a fifth of what it otherwise would be.

348. Air a Mixture

We have at least five good reasons for believing that air is not a chemical compound, but a mere *mixture* of nitrogen and oxygen, with small amounts of other gases:

1. *The composition of the atmosphere at any given place is not quite constant.* It also varies perceptibly with the elevation, being a trifle richer in oxygen and poorer in nitrogen at sea level than at elevations of a few miles. If air were a definite compound, its composition would be invariable. The highly rarefied air that exists at elevations above 60 or 70 miles probably contains appreciable quantities of hydrogen and helium.

2. *Air is readily separated into its components by fractional distillation of liquid air.* If it were a compound it would all distil over in a single fraction, at a definite temperature.

3. *Air placed in contact with water or other solvents is altered in composition,* for the components of the air differ in solubility (oxygen being nearly twice as soluble as nitrogen, under the same pressure). (Ex. 1.)

4. The *density and physical properties* of air are precisely those that would be inferred from the proportions and physical properties of its component gases. If a chemical change occurred in mingling these gases to form air, there would be a change in properties or a change in volume, or some other evidence of a chemical reaction. (Ex. 2.)

5. *No chemical formula can be written that will exactly account for the proportions in which nitrogen and oxygen are present in air.* The

nearest simple formula would be N_4O, but this would indicate far toc great a density for air, and the proportion of oxygen in air is slightly greater than this indicates. (Ex. 3.)

349. How the Composition of the Atmosphere Has Been Determined

The composition of air or any mixture of the gases contained in air may very readily be determined:

1. A sample is drawn into a gas buret (*B*, Fig. 118) and its volume noted. It is then transferred to a bulb *C*, containing a solution of potassium hydroxide, to absorb and remove carbon dioxide. The unabsorbed residue of gas is then returned to *B*, and the decrease in volume noted. This represents the *carbon dioxide* in the original sample.

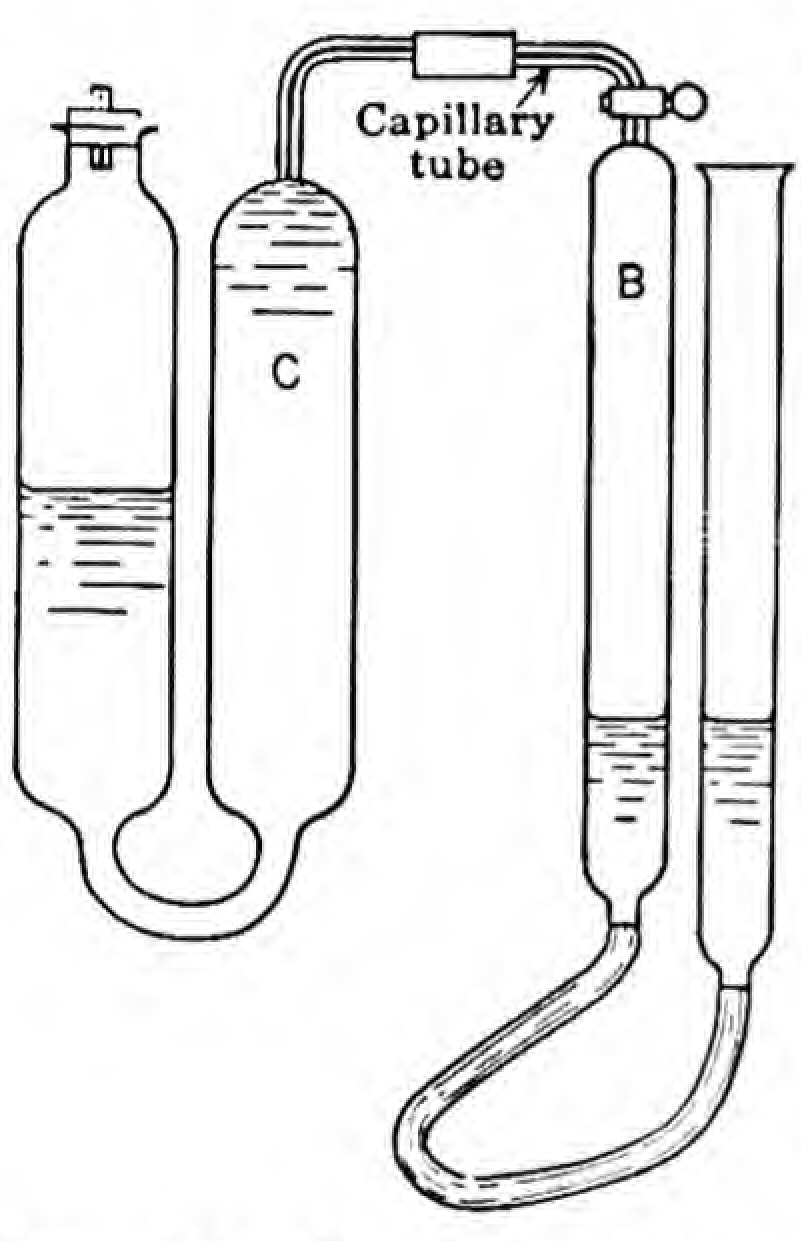


FIG. 118. Determining the composition of air.

2. The bulb *C* is next replaced by one containing some material that will absorb and remove oxygen. *Yellow phosphorus*, in the form of slender rods, wet with water, is an excellent absorbent, phosphorus being oxidized to the lower oxides of phosphorus, which then dissolve in the water. Or an alkaline solution of *pyrogallol* may be used. The air is passed from the gas buret, *B*, into the bulb containing the oxygen absorbent, is there shaken violently, then passed back into the gas buret. The process is repeated until no further decrease in volume is observed. The total decrease in volume represents the *oxygen* in the original mixture.

3. The residue in the gas buret now consists chiefly of *nitrogen*. A large sample of this mixture, carefully dried, is passed over heated magnesium. This combines with the nitrogen, forming magnesium nitride, Mg_3N_2 (§ 382). Argon and the other inert gases pass through unchanged. It was by this means that the presence of argon in the atmosphere was first detected (Ramsay and Rayleigh, 1895).

4. The final residue of inert gases has been analyzed by condensing a large sample in a liquid-air machine, followed by fractional distillation to separate the different components.

The composition of the atmosphere, determined as just described, fluctuates only slightly at the earth's surface, though oxygen may fall

below the normal amount by several tenths of a per cent, under unusual circumstances. The average composition of dry air at sea level is here given, in percentages:

	By Volume	*By Weight*
Nitrogen	78.03	75.58
Oxygen	20.99	23.08
Argon	0.93	1.28
Carbon dioxide	0.035	0.053
Hydrogen	0.01	0.001
Rare inert gases (§ 355)	0.0024	0.001

350. Accidental Components of the Atmosphere

The atmosphere also contains *accidental components*, in proportions that vary widely with the locality. Water vapor is the chief of these. There are likely to be traces of ammonia, sulfur dioxide, oxides of nitrogen, hydrogen sulfide, and many other gases, together with solid particles (dust) of many different sorts. Ozone is usually present in traces; in the atmosphere of London, for example, about 1 part in 100 million parts of air has been reported.

The solid particles in the air have frequently been collected, counted, and identified under the microscope. They consist of particles of soot (unburned carbon); particles of common minerals; ash particles that are sometimes chiefly magnetic iron oxide, and sometimes siliceous material; plant spores, and a few bacteria (normally only 4 or 5 bacterial spores in a liter, as contrasted with 6 to 20 million in a liter of unfiltered river water).

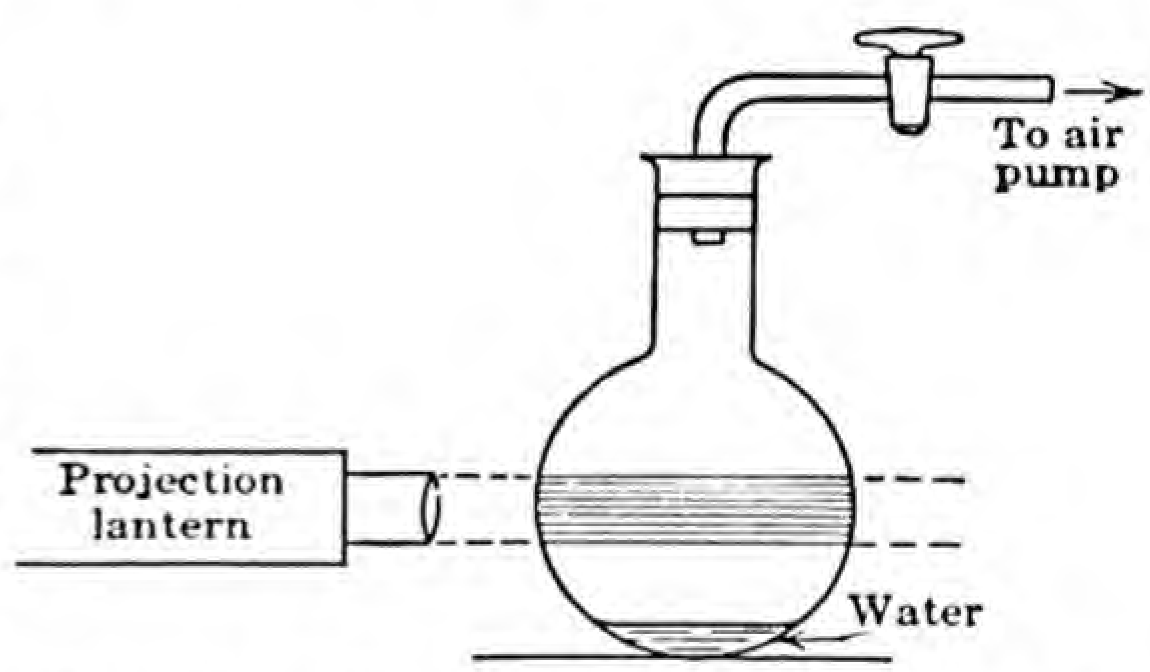


FIG. 119. Demonstrating the presence of dust and ions in ordinary air.

The dust in the atmosphere is responsible for many familiar natural phenomena. Dust particles and ions in the air serve as nuclei for the condensation of water vapor, forming the microscopic liquid droplets that constitute fog or clouds.

The formation of fog by the condensation of moisture on dust particles in ordinary air is easily shown when a beam of light in a darkened room is made to traverse a sample of air (Fig. 119). When the stopcock between the flask and the water pump is opened for a moment the moist air in the flask expands and is thereby cooled, becoming *super-*

saturated with moisture. If ordinary air is used the surplus moisture at once precipitates, gathering in liquid droplets about the dust particles to form a dense fog, in which the path of the light is brilliantly luminous. Air that has been freed from dust by being filtered through a wad of cotton gives no such effect.

If the atmosphere were completely free of dust and ions, moisture would condense directly from supersaturated air, onto the surfaces of our clothing. An air-tight raincoat in such a situation would afford us some protection, but umbrellas would be useless. The dust particles in the air are also responsible for reflecting toward the observer the shorter wavelengths of light that greet the eye in the russet or orange hues of sunrise and sunset.

351. Moisture in the Atmosphere

Moisture is subject to much greater fluctuations than any other component of the atmosphere. In temperate regions at least 100,000 tons of water vapor are often present in the atmosphere over each square mile of the earth's surface. In the tropics several times that amount may be present.

Air that contains as much water vapor as it can *acquire* and *retain* at the given temperature, *in contact with liquid water*, is said to be *saturated*. The water vapor in it then exerts a definite vapor pressure at each temperature (§ 151). If only half as much moisture is present as in fully saturated air, a given sample of air is said to have a *relative humidity* of 50 per cent.

From a table of vapor pressures (Appendix C) we may infer what proportion of all the molecules in a sample of air are molecules of water vapor, and also what total weight of water is present in a given volume of air of known temperature and relative humidity. At 21°C, for example, the vapor pressure of water is found to be 18.65 mm of mercury. If the relative humidity of a sample of air at 21°C is only 40 per cent, the partial pressure (§ 118) exerted by the water vapor is $0.40 \times 18.65 = 7.46$ mm. This is the pressure the water vapor would exert if it occupied the whole space alone, in the complete absence of air.

If the barometric pressure is 746 mm, the pressure of 7.46 mm exerted by the water vapor in the sample of air just considered is 1 per cent of the total pressure. From this we may infer that 1 molecule in every 100 is a molecule of water vapor (Dalton's Law of Partial Pressures, § 118).

Now a liter of water vapor (mol. wt. = 18), treated as an ideal gas, recalculated to standard conditions, weighs 18/22.4 grams. Under the

very much lower partial pressure and higher temperature of our sample, it will weigh proportionately less, namely $(18/22.4) \times (7.46/760) \times (273/294) = 0.0073$ gram. This is the actual weight of water vapor in a liter of air of the temperature and relative humidity specified. (Ex. 4–7.)

Water vapor in the atmosphere is completely invisible. So is *steam* (water vapor at high temperatures) when free from liquid droplets. *Clouds, fogs, mist,* and the visible part of the jet from a tea kettle or locomotive all represent *liquid water in microscopic droplets,* which in unsaturated air soon disappear by evaporation. The small size of the liquid particles forming a cloud or mist gives them enormous surface, relative to their mass, hence they encounter so much friction in falling that they hover in the air almost indefinitely.

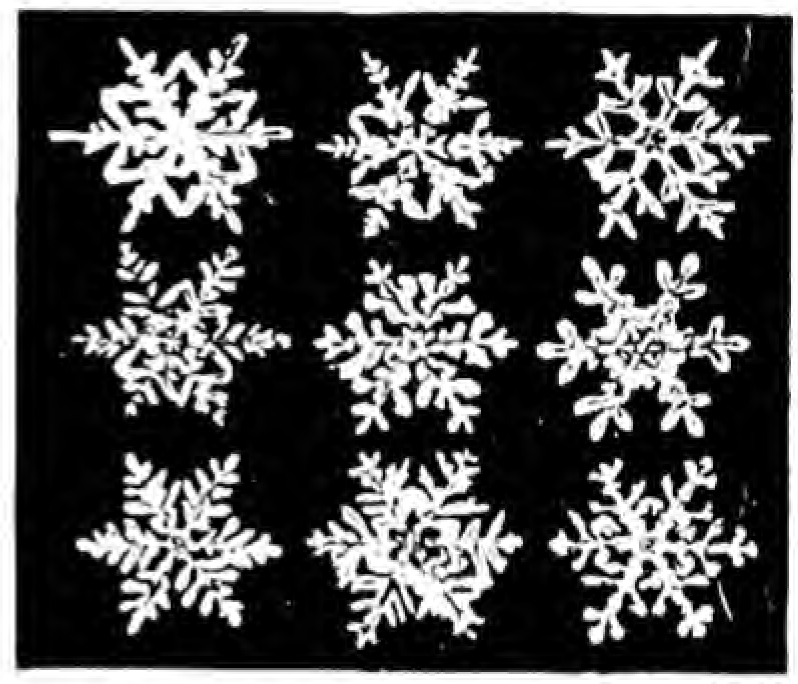


FIG. 120. Snowflakes.

The liquid droplets forming a cloud carry positive or negative charges, hence mutually repel one another. A bolt of lightning is frequently followed by a shower because it discharges the microscopic liquid droplets forming the cloud, so that their mutual repulsion is overcome and they coalesce to form drops large enough to descend as *rain.*

When raindrops descend through a layer of air sufficiently cold to freeze them as they fall, the result is *hail. Snowflakes* are formed by slow deposition of moisture about nuclei of dust or ions, from supersaturated air that has been cooled below the freezing temperature. Their comparatively slow growth favors the development of numberless beautiful figures, all with sixfold symmetry (Fig. 120).

352. Air Conditioning

The relative humidity of the atmosphere has quite as much to do with our comfort as the temperature. One can stand degrees of humidity in temperate and polar regions that would cause extreme discomfort or sunstroke in the tropics.

For Comfort at	*Relative Humidity Should Be About*
60°F	65 per cent
70°F	47 per cent
80°F	30 per cent
90°F	15 per cent

When homes are heated in the winter the humidity usually falls too low. Several gallons of water a day should be introduced into the air in circulation in the ordinary home in winter, to keep the humidity up to the standard or maximum comfort. The higher the humidity, the lower the temperature may be, within limits, without discomfort. Since comfort is attained at a lower temperature than would otherwise be possible, careful adjustment of the humidity saves fuel.

Fresh air for ventilating auditoriums and even office buildings and railroad coaches is frequently passed through a spray of water that serves to humidify it and remove dust and bacteria, and to cool it in the summer time. It is then freed from mist, and brought to an appropriate temperature and humidity before being admitted to the room through ducts in the walls or ceiling. This is the principle of *air conditioning.*

In spinning and weaving cotton cloth, in drying lumber, and frequently in storage of materials in warehouses the humidity of the atmosphere needs to be carefully regulated. Air may best be freed from moisture on a small scale by passing it through some desiccating agent, usually $CaCl_2$, P_2O_5, $Mg(ClO_4)_2$, or concentrated H_2SO_4. On a large scale in industry it is simply *cooled* to so low a temperature that most of the moisture it contains is frozen out as ice.

353. Ventilation

Air exhaled from the lungs is found to be very much depleted in oxygen and enriched in carbon dioxide:

	Oxygen	*Carbon Dioxide*
Inhaled air	20.9	0.03
Exhaled air	15.9	3.70

An adult person breathes about 17 cubic feet of air and exhales about 0.6 cubic foot of carbon dioxide each hour.

It used to be supposed that the injury done by confining people in an insufficient supply of air was due to the depletion of oxygen. It is now known that air containing 17 per cent oxygen will support life, though it will not support combustion. Another theory, now abandoned, was that crowds exhale subtle poisons. Repeated search has failed to reveal any.

We can readily account for the discomfort that is experienced in confined air, and the illness and death that overcame victims crowded together in the Black Hole of Calcutta and similar situations, when we

recall that heat is continuously liberated within the body by the oxidation of organic compounds. The body must get rid of its surplus heat (1) by radiation and conduction into the surrounding air, and (2) by evaporating moisture at the surface of the body. The high temperature of the air in a crowded room decreases the rate at which bodies surrounded by it lose heat by direct conduction; its high humidity decreases the rate at which moisture can evaporate into it. Through an increased rate of respiration and increased perspiration the lungs and sweat glands of persons breathing confined air make an effort to get rid of heat in spite of the handicaps of high temperature and high humidity, but are placed under a strain that may result in illness and death.

Since carbon dioxide is not the source of danger in crowded rooms, it may seem illogical to use its percentage in the air as a measure of the quality of ventilation. Yet experience shows that in crowded rooms that are comfortable and well ventilated the percentage of carbon dioxide does not rise above about three times its normal amount, or above about 0.1 per cent; hence ventilation engineers have often set this as the permissible upper limit for carbon dioxide in auditoriums. To make sure that carbon dioxide does not exceed this percentage at least 1000 cubic feet of fresh air must be furnished for each person each hour. This means that fresh air equal to the cubical contents of a crowded room [1] must be supplied every 10 or 15 minutes. (Ex. 8.)

354. Liquid Air

Liquid air was first prepared commercially just before the beginning of the present century. It is important as a source of low temperatures (down to about $-200°C$) in experiments that have sought to determine the behavior of materials of all sorts at temperatures far below those ordinarily encountered. It also serves in a preliminary cooling of hydrogen and helium that is the first stage in liquefying and solidifying these gases.

Liquid air is important as the commercial source of *nitrogen* for the production of ammonia by the Haber process (§ 366) and as the commercial source of *oxygen* for cutting and welding metals (§ 62). Argon, neon, and other inert gases (§ 355) are also obtained by fractional distillation of liquid air.

Different methods for the liquefaction of air all follow the same general plan:

[1] Not counting air above a height of about 12 feet.

1. The air is first freed from dust, moisture, and carbon dioxide, then compressed with powerful pumps. The heat liberated in the compression is removed by passing the compressed air through a cooling coil, surrounded by running water.

2. The air is next permitted to expand through a valve, doing work as it expands *in overcoming the attraction of its own molecules for one another* (Linde process); or it is made to do work *in driving an engine*, which can be made to compress a new portion of purified air (Claude process). But because energy in the form of heat energy is expended in the performance of work, the temperature of the expanded air is very much less than that of the incoming air.

3. Finally, the cold expanded air passes around the outside of a set of tubes through which a new portion of compressed air is entering. The incoming air is thus cooled, and in expanding, doing work, is cooled still more. The temperature thus falls lower and lower, until a part of the air condenses to a liquid and collects in a receiver.

355. The Inert Gases (Group 0 of the Periodic Table)

Symbol	*Atomic Number*		*Melting Point* (°C)	*Boiling Point* (°C)	*Volumes in 1,000,000 Volumes of Air*
He	2	Helium	< −272.2	−268.9	3
Ne	10	Neon	−248.5	−245.9	12
A	18	Argon	−189.3	−185.7	9400
Kr	36	Krypton	−156.6	−152.9	0.5
Xe	54	Xenon	−112	−107.1	0.06
Rn	86	Radon	−71	−61.8	

For general characteristics of the inert gases refer to §§ 213, 237.

Helium, the lightest of the inert gases, was discovered by means of the spectroscope in the atmosphere of the sun, many years before it was found on earth. It occurs in cavities in some rare minerals and in a few mineral springs; but its most important source is the *natural gas wells* of Kansas and Texas, which contain up to 2 per cent of helium. The government plant erected for the production of helium, for filling dirigible balloons, condenses the more volatile components of the natural gas in liquid-air machines, then by fractional condensation separates the helium from the residue.

Helium is the only gas which is light enough to compete with hydrogen in buoyant effect, and has the inestimable advantage of being completely incombustible. (Ex. 9.) Helium is the most difficult substance to liquefy and solidify. It is used as a substitute for nitrogen in

the compressed air supplied to workmen tunneling under rivers. The lower solubility of helium as compared with that of nitrogen very much decreases the risk that a too sudden return from the high-pressure chambers to ordinary atmospheric pressure may release air bubbles in the blood and spinal fluid, either crippling or killing the workmen.

A few unstable compounds of helium with metallic elements (Hg, Fe, Pd, Pt, U) perhaps exist.

Neon is contained in traces in the less readily condensable portions of the atmosphere. An electric current passed through rarefied neon gives a red light, used in electric signs. The neon is ionized (Ne^+) by electrons emitted from the cathode, then the ions carry the current. The red light represents radiant energy released by individual atoms, as a displaced outer electron reverts to a lower energy level (§ 234). The color of the light emitted by an electric display sign of this type depends in part on the color of the glass of which the tube is made, and in part on the nature of the gas or vapor that it contains. Different mixtures of argon, neon, hydrogen, mercury vapor, and sodium vapor, in combination with different sorts of glass, give a very wide range of colors. Details of a neon-sodium vapor lamp are given in Fig. 168, p. 620.

Argon resembles nitrogen very closely in boiling point and other physical properties, but is distinguished chemically by its nearly complete inability to combine with other elements. At the present time, argon is used only for filling incandescent light bulbs. Its purpose is to reduce the rate at which metallic vapor evaporates from the filament and is deposited on the inner walls of the bulb. Metallic atoms that do leave the filament collide with atoms of argon and are frequently turned back. Nitrogen has been used for this purpose instead of argon, but is a better conductor for heat, hence results in lowered filament temperature and consequently in lowered efficiency as an emitter of visible light.

Argon combines with 1, 2, 3, 6, 8, or 16 molecules of boron trifluoride, the second of these being most stable. It also forms one or more unstable hydrates, as do krypton and xenon.

Krypton and *xenon* occur only in very small quantities in the atmosphere. If the molecules of ordinary air were to file past an observer at the rate of one each second, he would see an argon molecule once every two minutes, on the average; but a krypton molecule only once in about three weeks, and a xenon molecule only once in over six months.

Niton, or radium emanation, now called ***radon***, is a radioactive gas, formed by disintegration of radium, the other product being helium, (§ 224).

For a review of this chapter see Exercises 10–22.

Technical Words

Saturated air, p. 402.

Supersaturated air—air that contains more moisture than saturated air at the given temperature. The surplus moisture, in absence of dust particles or ions, may be retained for a very long time, but is gradually precipitated on the walls of the containing vessel.

Relative humidity—the ratio of the weight (or partial pressure) of the moisture in a given sample of air to that in fully saturated air, at the same temperature.

Exercises

1. How does the weight of gas dissolving in a liquid vary with the pressure applied?

2. From the proportions by volume (to the nearest per cent) of the three most plentiful components of the air (§ 349) and their molecular weights, calculate the average molecular weight of the gases of the atmosphere. 290

3. What density would air possess under standard conditions if it were a compound with the formula N_4O? 321

4. The vapor pressure of water at 29°C is 30 mm. A sample of air at this temperature has a relative humidity of 60 per cent. What pressure does the water vapor in this air exert? Under a total pressure of 720 mm what percentage of the pressure is exerted by the water vapor? 180, 250

5. In the sample of air just considered, how many molecules of water vapor are present for every 100 molecules in the mixture? What is the mole-fraction of water vapor? 250

6. Eighteen milligrams of water vapor are present in a total volume of 4.48 liters of moist air, under standard conditions. How many moles of water vapor is this for one mole of total (air plus water)? What is the mole-fraction of water vapor? 500

7. In the sample of air just considered, what fraction of the total pressure exerted by the air is due to the water vapor? What is the actual pressure of the water vapor in millimeters? What is the relative humidity of this sample of air, if the vapor pressure of water at 0°C is 4.58 mm? 500, 380, 830

8. The cubical contents of a room 20 feet square and 8 feet high is renewed every 10 minutes. For about how many persons will this supply sufficient ventilation? 190

9. The buoyant effect of any gas in a balloon is proportional to the difference between its density and that of the surrounding air, hence to the difference between its molecular weight and that of the surrounding air. From the molecular weights of hydrogen and helium, in comparison with the average molecular weight of the gases of the air, determine by what percentage the buoyant effect of hydrogen exceeds that of helium. 800

10. What arguments based on physical properties prove that air is a mixture?

11. Name two materials commonly used to combine with oxygen, in determining the percentage of oxygen in the atmosphere.

12. Mention some natural phenomena that depend on the presence of dust in the air.

13. Explain how one may determine the pressure exerted by the moisture in air of known relative humidity and temperature.

14. Explain how the mole-fraction of each component of the atmosphere may be inferred from its percentage by volume.

15. Under what conditions may air be supersaturated with moisture?

16. Explain why high relative humidity makes the atmosphere uncomfortable.

17. What is accomplished by passing air through a spray of water, in air conditioning? What must then be done to the air before admitting it to the building?

18. How may air best be freed from moisture, on a small scale in the laboratory, and on a large scale in industry?

19. Indicate three successive steps commonly met in any process for producing liquid air.

20. What is the commercial source of helium?

21. Explain how neon is caused to emit red light in electric signs.

22. Which do you think is the larger, the number of people on earth or the number of molecules of xenon (§ 355) that are contained in the atmosphere of a large lecture hall? Show what assumptions you make in your estimate, and how you use them.

Chapter 27

NITROGEN

356. Comparing Nitrogen with Oxygen and Fluorine

Let us begin our survey of nitrogen by comparing it with two other non-metals already studied, occupying the two places next toward the right in the Periodic Table:

Column in Periodic Table	5A	6A	7A
Formula	N_2	O_2	F_2
Valence electrons in each atom	5	6	7
Electrons to be gained for an octet	3	2	1
Inferred bonding	$\equiv$	$=$	—
Heat of dissociation (kilocalories)	170.2	118.2	30 (estimated)
Interatomic distance (Å)	1.114	1.204	1.45
Expected distance (§ 249) for type of bonding indicated	1.10	1.18	1.28

We notice that each nitrogen atom needs to gain 3 electrons, or a half-share in 3 pairs of electrons, to complete its outer octet (§ 239). Thus when 2 nitrogen atoms combine to form a molecule, we would expect 3 pairs of electrons to be shared, thus forming a triple bond (§ 249) between the two atoms, as in :N⋮⋮N: , otherwise written N≡N.

But each atom of oxygen needs to gain only 2 electrons or a half-share in 2 pairs of electrons to complete its octet; and each atom of fluorine needs to gain only 1 electron or a half-share in 1 pair of electrons to complete its octet. We infer that the oxygen atoms in O_2 are linked by a double bond (or by something nearly equivalent, from the standpoint of energy) and that the fluorine atoms in F_2 are linked by a single bond.

All this is based on the assumption that the atoms just considered really do form octets when they combine in pairs to form molecules. Our anticipation is confirmed by measuring the *heat of dissociation*, in other words, the heat that disappears or the energy that must be expended, in dissociating ($N_2 \rightarrow 2N$) the molecules of one mole of gas into their component atoms. We find that this is least for F_2, is roughly

multiplied by four in passing to O_2, and is greater still for N_2. This is evidence that the atoms in F_2 are weakly bonded, those in O_2 are much more strongly bonded, and those in N_2 are still more strongly bonded (presumably a triple bond). Evidence based on the absorption spectrum of elementary oxygen seems to indicate that the bond between its two atoms, instead of being an ordinary double bond, is something rather unusual, perhaps a single bond, associated with two 3-electron bonds, as expressed by $\mathrm{O}\overset{\cdots}{\underset{\cdots}{-}}\mathrm{O}$.

As the bonding gets stronger and stronger, the atoms are drawn more and more closely together. Our table shows that the *interatomic distance* (center-to-center distance between adjacent atoms) decreases steadily in passing from F_2 to O_2 to N_2.

357. Influence of Bonding on Chemical Activity

We can now explain some of the most striking differences between the three non-metals just considered. If they are to react with any other element we must overcome the attraction of the paired atoms for each other. It is relatively easy to do this for the singly bonded molecule F_2; hence fluorine is chemically *extremely active*. It is much more difficult for the molecule O_2; hence oxygen is *far less active* than fluorine. It is still more difficult for the triply bonded molecule N_2; hence nitrogen is *relatively inert*. To rouse its molecules into action we need to bring enough energy to bear to break down the triple bond—in an electric arc or a flash of lightning (§ 362), or by reaction with a very active metal, such as lithium or magnesium (§ 382).

More than this, we see that fluorine readily forms the fluoride ion, F^-, since each atom needs to gain only 1 electron to complete its octet. But the oxide ion, O^{--}, is formed less readily, since 2 electrons need to be gained, and the second one in spite of a repulsion exerted by the first. The nitride ion, N^{---}, for the same reason, is formed less readily still. The active metals (Li, Mg, Al, etc.) form ionic fluorides, oxides, and nitrides; but the heavy metals (Fe, Zn, Pb, etc.) tend to form covalent compounds, particularly with nitrogen.

358. Occurrence of Nitrogen

1. An inexhaustible supply of elementary nitrogen is found in the *atmosphere*, which is about three-fourths nitrogen by weight. This is more than 20,000,000 tons of the element for each square mile of the earth's surface.

2. Great deposits of *sodium nitrate* and *calcium nitrate* occur in various parts of the world, notably in Chile and South Africa. The

Chilean sodium nitrate beds are more than 200 miles long, and average 2 miles wide and 5 feet thick. The crude material contains 20 to 60 per cent $NaNO_3$ (often called Chile saltpeter) and is recrystallized in great open basins, where evaporation takes place by the heat of the sun.

3. Nitrogen is found in all plant and animal matter, in the gelatinous material called *protoplasm*, which lines the walls of living cells. This is the seat of the chemical activities of life. Nitrogen compounds called *proteins* make up most of the weight of dry meat, and related substances compose gelatin, horn, feathers, and hair. Most plants absorb nitrogen chiefly as nitrate, and by a process of reduction bring it into union with carbon and hydrogen. Animals lack the ability to do this, but must obtain their essential nitrogen compounds, nearly ready made, from plants or other animals.

359. Physical Properties of Nitrogen

	N_2	O_2	F_2
Melting point	$-210.5°$	$-218°$	$-223°$
Boiling point	$-195°$	$-182.7°$	-188.2
Solubility in water (volume, under standard conditions, in 100 vol. of water)	2.35	4.9	(Reacts)

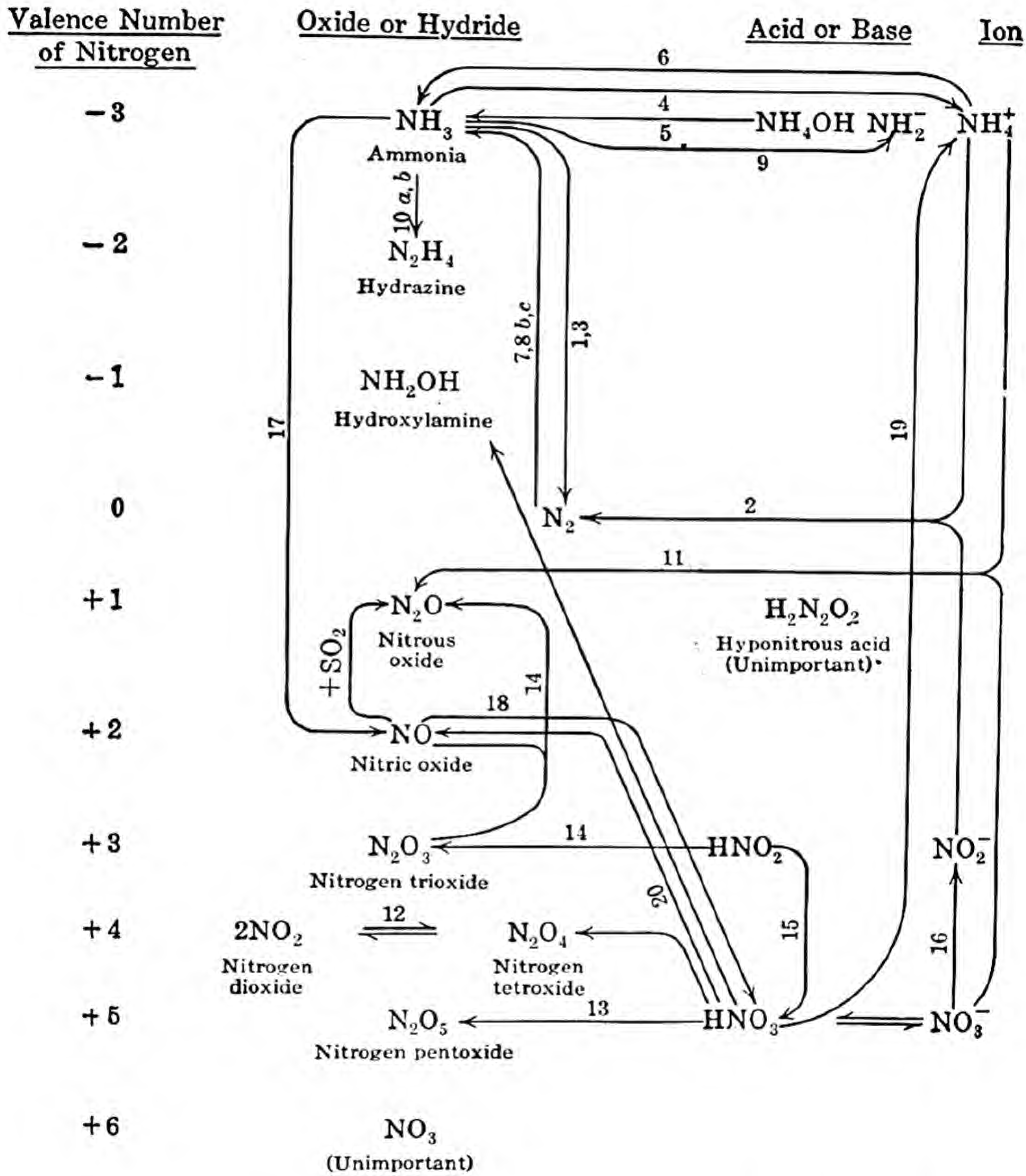
Nitrogen liquefies and solidifies only at very low temperatures. That this is true of oxygen and fluorine as well as nitrogen is evidence that atomic radius (small for all three elements) is of more importance in determining boiling point than the special bonding in O_2 or the triple bonding in N_2, as compared with the single bonding in F_2. The only two elements having a lower boiling point than nitrogen are hydrogen ($-252.7°C$) and helium ($-268.9°C$), which are the only gaseous elements that possess a very much smaller atomic radius than nitrogen (see table in § 252).

The small attraction that nitrogen molecules exert upon neighboring molecules of whatever kind enables us to predict that nitrogen must be *very slightly soluble* in water or any other solvent—even less soluble than oxygen. That the gas is *odorless* follows from the fact that it is chemically inert.

The diatomic molecules, characteristic of nitrogen, oxygen, or fluorine in the gaseous state, persist even in the liquid and solid states. Since the electrical force that such molecules can exert upon one another is never very great, even when they are closely packed together, the solid element forms soft, weak *molecular crystals* (§ 143).

360. Valence States of Nitrogen

Nitrogen, in its most important compounds, displays all the valence states between −3 (in ammonia and ammonium salts) and +5 (in



nitrogen pentoxide, nitric acid, and the nitrates). In nitrogen superoxide, NO_3, it even has the valence state +6. The most important reactions of nitrogen are those here indicated by numbered arrows, which the reader should compare with the correspondingly numbered equations of this chapter.

361. Preparation of Elementary Nitrogen

Elementary nitrogen (containing a little argon as its chief impurity) may readily be prepared by freeing air from dust and carbon dioxide, then passing the residue over some material that will combine with and remove oxygen. We have already told how this is accomplished in the analysis of small samples of air (§ 349). Among laboratory methods for preparing nitrogen, on a somewhat larger scale, we may mention three:

1. Air is bubbled through a solution containing *ammonium chloride and ammonium hydroxide in the presence of copper turnings* (Fig. 121). The copper is oxidized, forming a blue solution of tetrammine cupric

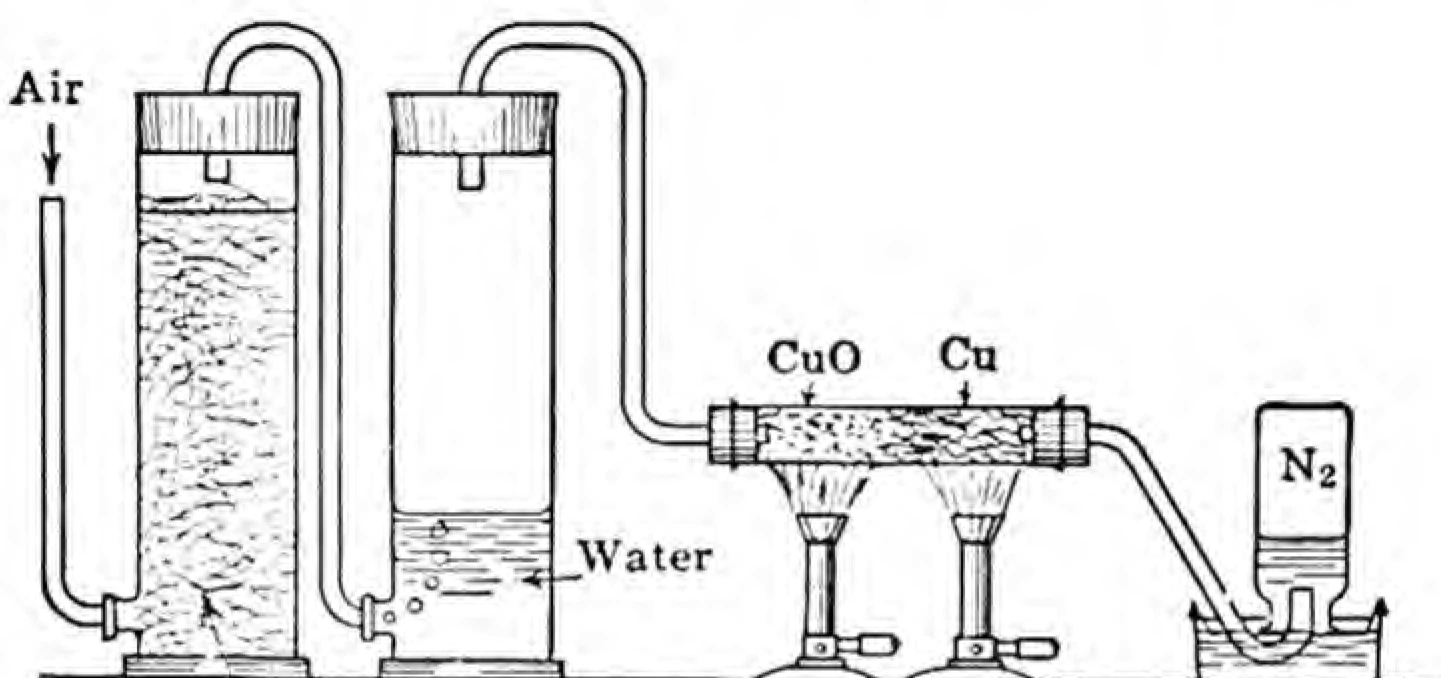


FIG. 121. Laboratory preparation of nitrogen from air.

hydroxide (§ 364). The residue, thus deprived of most of its oxygen, is bubbled through water to remove most of the ammonia gas that it has acquired in the previous treatment. It is then passed through a tube containing *heated cupric oxide*, to oxidize any remaining ammonia (forming free nitrogen and water), and finally over *heated copper turnings*, to remove any remaining trace of oxygen. It is collected over water, as shown in the sketch, or is dried and passed directly to its intended application. (Ex. 1.)

2. Air may be bubbled through a solution of *ammonium hydroxide* (density about 0.94), then led over *heated cupric oxide*, followed by *heated copper turnings*. Under these conditions the ammonia gas yielded to the air by the ammonium hydroxide solution is sufficient to combine with practically all the oxygen in the air:

Equation 1: $$2NH_3 + 1\tfrac{1}{2}O_2 \rightarrow N_2 + 3H_2O$$

To the nitrogen thus obtained is added that originally contained in the current of air. (Ex. 2.)

3. To obtain *pure nitrogen,* free from the argon, ammonium salts may be oxidized by any one of several oxidizing agents. Commonly, a solution of ammonium chloride is slowly added to a warm solution of sodium nitrite:

Equation 2: $NH_4Cl + NaNO_2 \rightarrow NaCl + N_2\uparrow + 2H_2O$

or, as an ionic equation:

Equation 2(*a*): $NH_4^+ + NO_2^- \rightarrow N_2\uparrow + 2H_2O$

(Ex. 3.)

4. Commercially, on a grand scale, several million tons each year, nitrogen is now obtained from *liquid air.* Most of this is used in the synthesis of ammonia (§ 366).

362. The Nitrogen Cycle

Nitrogen, in nature, passes through a definite cycle of changes, outlined in Fig. 122:

1. *Nitrogen fixation by lightning.* Careful experiments have shown that all the nitrogen required for the growth of the higher plants is absorbed through their roots, as nitrogen compounds—chiefly nitrates. Our study of the cycle of nitrogen in nature must therefore begin with processes that *fix* nitrogen, namely cause it to combine with other elements.

There are several processes in nature that bring nitrogen into combination with other elements. Every lightning flash causes a little of the nitrogen of the atmosphere to unite with oxygen, to form *nitric oxide,* NO (§ 374). This reacts with oxygen and water (§ 379) to form *nitric acid,* which reacts with the limestone of the soil to form *calcium nitrate.* (Ex. 4.)

2. *Nitrogen fixation by bacteria.* Although the higher plants are seemingly quite unable to make use of the nitrogen of the atmosphere, many bacteria do so readily. These are the *nitrogen-fixing bacteria,* the most famous of which are those that produce the swellings or nodules on the roots of certain leguminous plants (cow-peas, clover, and alfalfa).

Wherever leguminous plants grow luxuriantly their roots will be found covered with nodules, from the size of a pin point to the size of a man's thumb. Under the microscope, the nodules are discovered to be modified rootlets, in which many cells are swarming with bacteria. One might readily consider such an invasion of bacteria to be a menace

to the very existence of a plant. Yet, strange to say, the legumes that have been infected always grow much more luxuriantly than those that have not.

Details of what happens in this *symbiosis* are not very well known. It is nevertheless evident that the leguminous plant, with the aid of solar energy, builds up more carbohydrates than it needs. So the plant offers its surplus carbohydrate to the bacteria, which derive energy by breaking carbohydrate down. In return the bacteria bring atmospheric nitrogen into combination with other elements to form nitrogen compounds, which are handed over to the plant.

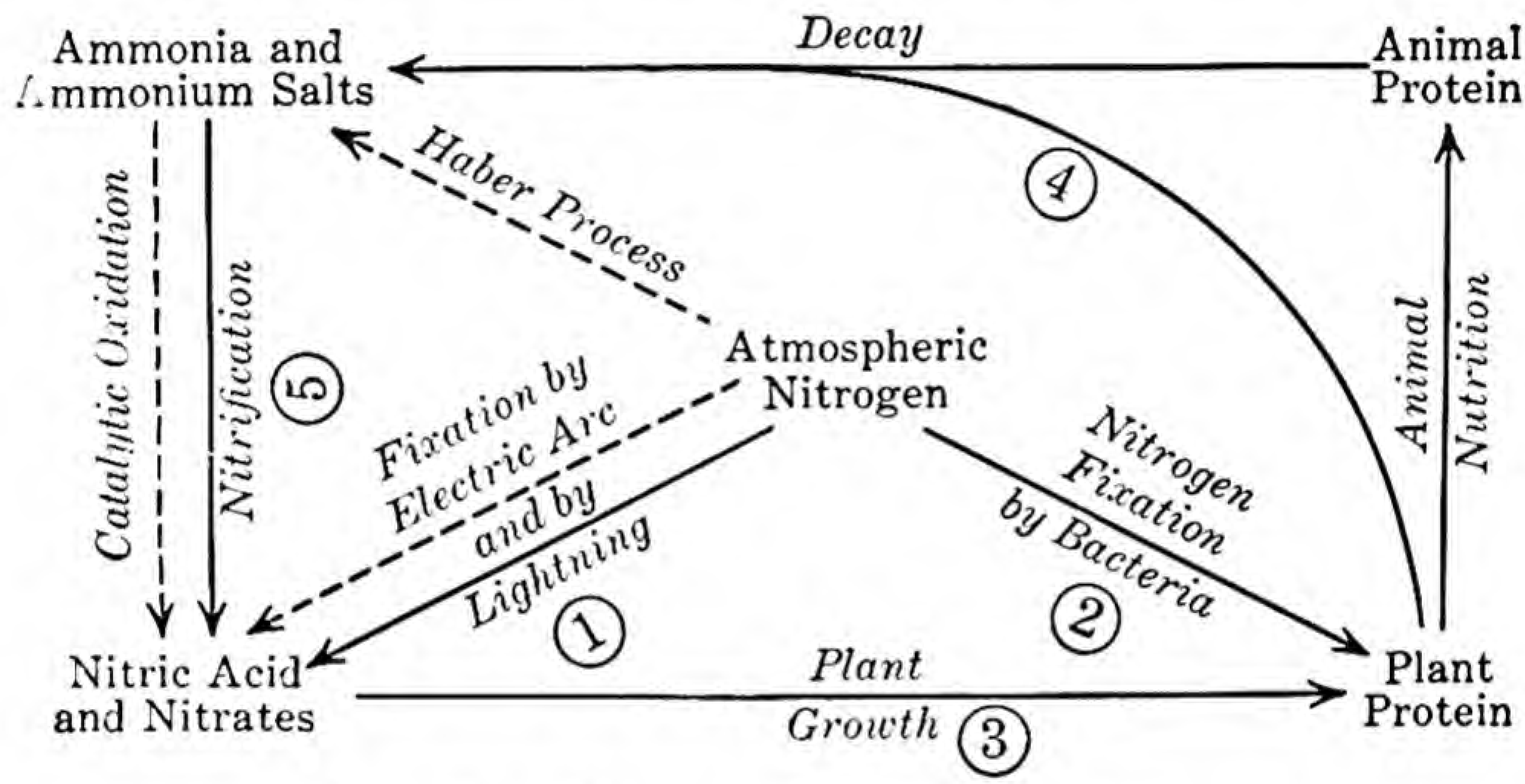


FIG. 122. The cycle of nitrogen in nature.

3. *Plant growth.* Nitrogen compounds, chiefly nitrates, absorbed through the rootlets of growing plants, are transformed into plant protein, which serves as food for animals and becomes animal protein. In this sentence we summarize highly complicated processes, the details of which are still very incompletely understood. It is as if we said that a factory absorbs steel, felt, wood, and ivory, and converts these materials into pianos.

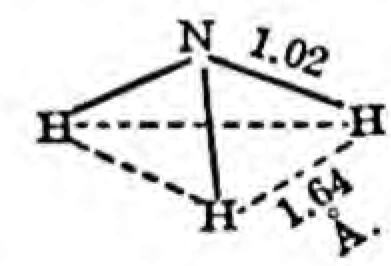
4. *Ammonification.* When plants and animals decay, their nitrogen is converted into ammonia or ammonium salts by the *ammonifying bacteria.*

5. *Nitrification.* Ammonium salts are not readily absorbed by most plants. The fact that we can use them (or even calcium cyanamide, § 367) as fertilizers is due to the fact that most soils contain *nitrifying bacteria*, which oxidize ammonium salts to form *nitrites* (which are poisonous to plants) and then to *nitrates* (which are an acceptable plant food). (Ex. 5.)

The cycle of nitrogen is thus repeated endlessly, and every atom of nitrogen in our own bodies may have passed through plants and animals, not once, but many times. Were this cycle broken, life upon the earth would soon cease. Some of the most important problems before the chemists of today concern the development of new or better ways of fixing nitrogen, or of preventing it, once fixed, from returning to the atmosphere.

363. Physical Properties of Ammonia

Ammonia, NH_3, is a colorless gas of characteristic odor. It is easily condensed to a colorless liquid (a pressure of 8.5 atmospheres being sufficient at 20°C). We have already mentioned properties of liquid ammonia that fit it for use as a refrigerant.



The infrared spectrum of ammonia, supplemented by the electron diffraction method, indicates that the ammonia molecule is a flattened tetrahedron, with the nitrogen at the apex, as shown in the margin of this paragraph. Comparing the electronic formula of ammonia, $\begin{array}{c}\mathrm{H}\\ \cdot\cdot\\ \mathrm{H{:}N{:}}\\ \cdot\cdot\\ \mathrm{H}\end{array}$, with that of water, $\begin{array}{c}\cdot\cdot\\ \mathrm{H{:}O{:}}\\ \cdot\cdot\\ \mathrm{H}\end{array}$, we observe a close resemblance, including the presence of unshared electron pairs (§ 250). The two substances are alike in such physical characteristics as *high specific heat, high heat of evaporation* (§ 155), and *association* (§ 123) in the liquid state. Both dissolve a great many ionic substances to form solutions that are good conductors of electricity. Their chemical reactions, as we shall see, are very similar.

364. Chemical Properties of Ammonia

1. Ammonia is *readily dissociated by heat*, yielding elementary nitrogen and hydrogen:

Equation 3: $$2NH_3 \rightarrow N_2 + 3H_2$$

This result seems chiefly due to the fact that nitrogen atoms have a strong tendency to combine in pairs to form stable molecules, N_2. Thus the collision of swift-moving molecules of ammonia at high temperatures produces molecules of nitrogen and sets hydrogen free.

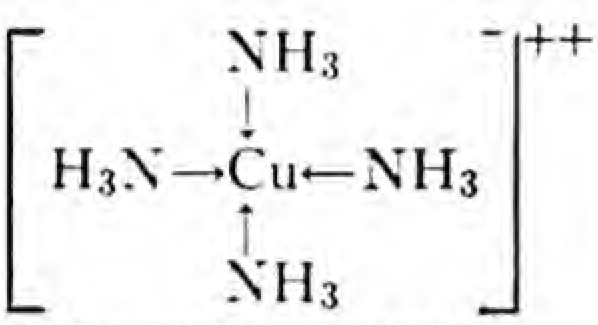
2. The unshared pair of electrons in the ammonia molecule enables it to act as a *proton acceptor* or *base* (§ 192) in the presence of substances

(*acids*, § 191) that are able to yield protons. The ammonia molecule, NH_3, accepting a proton, becomes the ammonium ion, NH_4^+:

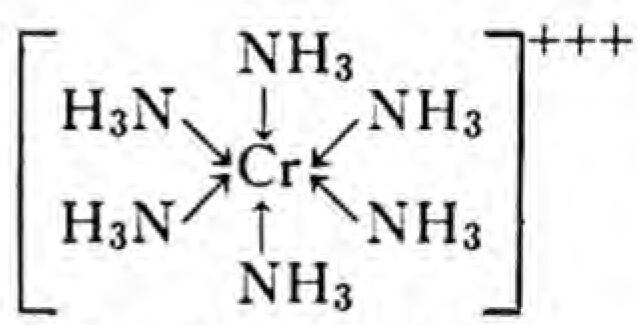
Equation 4: $$\overset{\mathrm{H^+}}{\mathrm{NH_3 + HCl}} \rightarrow \mathrm{NH_4^+ + Cl^-}$$

Thus we account for ammonium salts. (Ex. 6.)

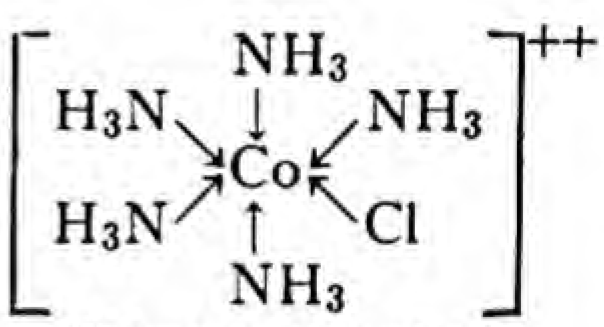
3. The unshared pair of electrons in the ammonia molecule may be donated to another molecule or to an ion, in forming a coordinate or semi-polar bond (§ 250). Thus we account for the union of ammonia with water to form *ammonium hydroxide*, NH_4OH, and for its union with heavy-metal cations to form complex cations called *ammines*. Examples:



Tetrammine cupric ion



Hexammine chromic ion



Chloropentammine cobaltic ion

Some ammines are so stable that they will withstand treatment with concentrated sulfuric acid without their ammonia being removed. Union of ammonia molecules, NH_3, with a cation, of course, does not alter the charge on the cation; but in the last example observe how cobaltic ion, Co^{+++}, by combining with one or more anions, such as Cl^-, in our example, may have its charge reduced or even reversed.

Hydrated cations, already described (§ 250), are analogous to the ammines; the only difference is that water, instead of ammonia, is combined with the central cation.

4. Ammonia, in the presence of a catalyst of finely divided platinum, is *readily oxidized to nitric oxide*, NO, which is itself easily converted into nitric acid (§ 379).

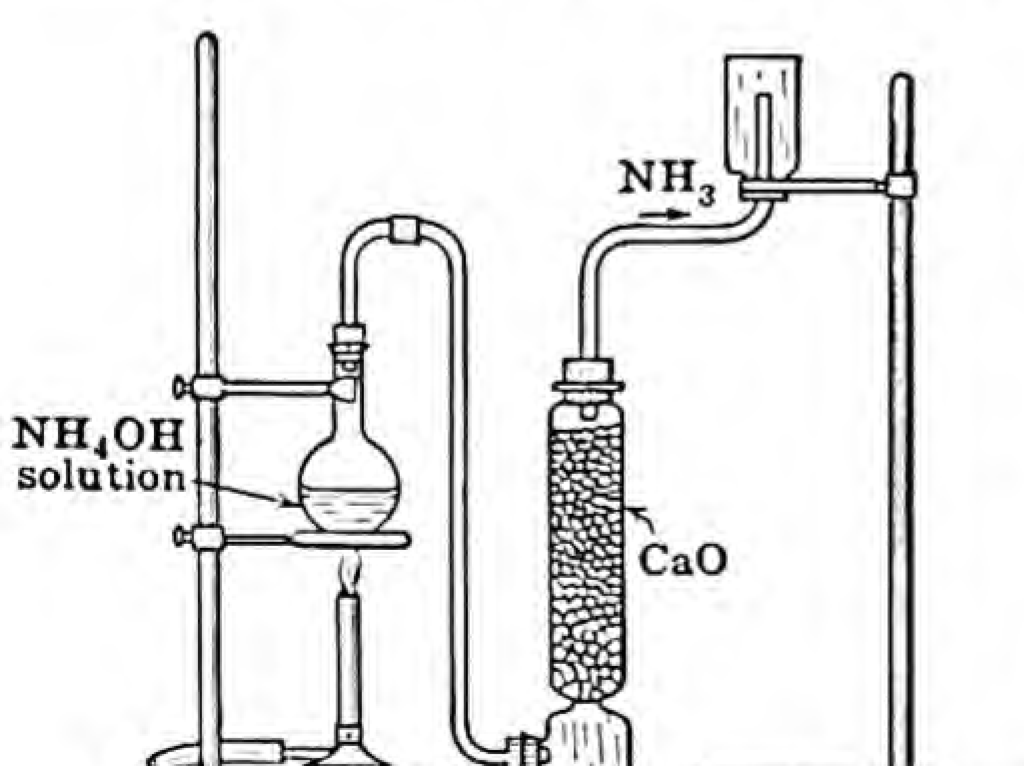


FIG. 123. Preparation of ammonia as a lecture demonstration.

365. Preparation of Ammonia

1. *As a lecture experiment*, ammonia is most readily prepared by heating a strong solution of ammonium hydroxide, drying the gas thus produced by passing it over quicklime, as in Fig. 123:

Equation 5: $$\mathrm{NH_4OH \rightarrow NH_3\uparrow + H_2O}$$

2. *In the laboratory*, ammonia is ordinarily prepared by heating a finely powdered ammonium salt with powdered sodium hydroxide or calcium hydroxide (or a mixture of the two, often called *soda-lime*):

Equation 6: $NH_4Cl + NaOH \rightarrow NH_3 \uparrow + NaCl + H_2O$

3. *Commercially*, on a grand scale, ammonia is usually prepared by direct union of hydrogen and nitrogen in the *Haber Process*, next described.

366. Synthetic Ammonia (The Haber Process)

The direct union of nitrogen and hydrogen to form ammonia is a reversible reaction and therefore incomplete:

Equation 7:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + 26.74 \text{ kilocalories } (400°\text{C, } 100 \text{ atm})$$

We have already (§§ 346, 347) noticed the conditions that must be observed in producing ammonia commercially by this method:

1. Since the reaction is reversible, an excess of hydrogen would be needed if we wished to secure the most complete transformation possible of the nitrogen into ammonia (Principle of Mass Action, § 338). In practice, the effort is rather to secure *the highest possible proportion of ammonia in the reaction mixture, at equilibrium.* This demands that hydrogen and nitrogen be used in the proportions by volume that are shown by the equation.

2. Since the reaction, at ordinary temperatures, is one in which heat is set free, the *reaction must be carried out at the lowest temperature at which a satisfactory reaction rate may be obtained*, with the aid of an effective catalyst (Principle of Van't Hoff, § 346).

It happens that the heat liberated in the synthesis of a mole of ammonia, under high pressures, decreases steadily with increasing temperature, and becomes zero at about 1200°C. Above this temperature heat disappears, hence the formation of ammonia, above 1200°C, becomes more and more nearly complete the higher the temperature. If temperatures of perhaps 2000°C were technically possible we should doubtless see them employed in the synthesis of ammonia; and we can now understand why ammonia is shown by the spectroscope in the atmosphere of the sun, in spite of a temperature of about 6000°A.

3. Since the synthesis of ammonia results in a decrease in the total number of molecules, and hence in a decrease of pressure, it is most nearly complete under *high pressure.*

4. An effective *catalyst* does not increase the yield obtainable at equilibrium at the given temperature, but it does insure that the transformation, during the short period that the gases are in contact with the catalyst, shall more nearly approach that attained at equilibrium.

An outline of the process, showing how the residue of untransformed nitrogen and hydrogen is recirculated, is shown in Fig. 124.

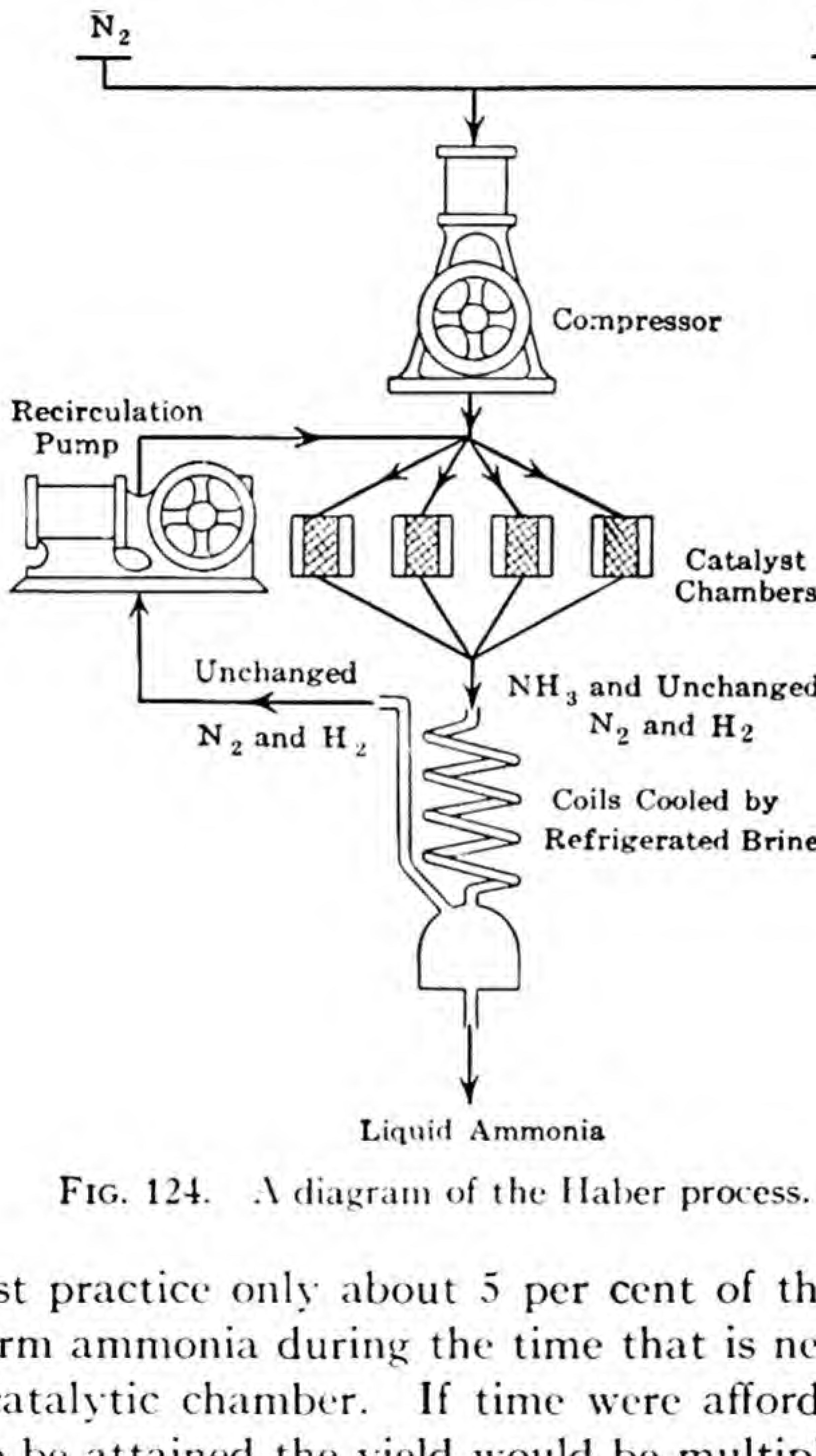


FIG. 124. A diagram of the Haber process.

Under the best practice only about 5 per cent of the reactant gases combine to form ammonia during the time that is needed for passing through the catalytic chamber. If time were afforded for complete equilibrium to be attained the yield would be multiplied several fold. (Ex. 7.)

Ordinarily, the union of the two gases is brought about at a temperature of about 500°C, under a pressure of about 200 atmospheres; but in some modifications, pressures as high as 950 atmospheres may be used. An important incident in the development of the process was the discovery that reaction chambers of low-carbon chrome-vanadium steel will retain hydrogen under high pressures, even at a dull

red heat, whereas ordinary steel, under such conditions, permits hydrogen to escape through pores in the metal about as freely as water through a sponge. The catalyst chamber of chrome-vanadium steel is shown in cross section in Fig. 125.

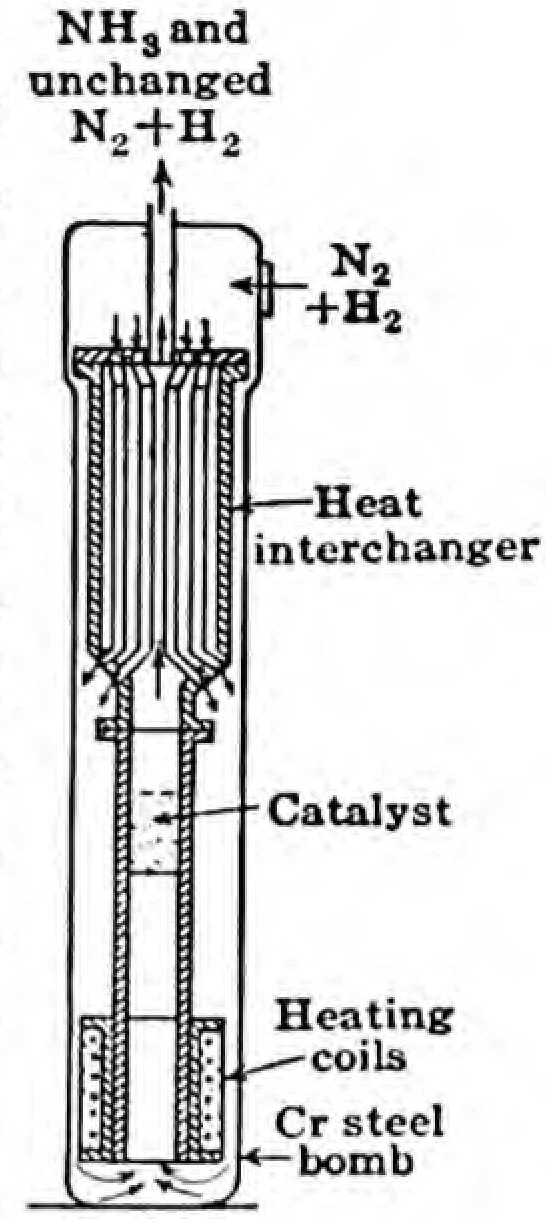


FIG. 125. Catalyst chamber for the synthesis of ammonia. Observe that the resultant mixture of gases, escaping upward from the catalyst, is cooled by being passed through a heat interchanger, in which they yield heat to the current of incoming nitrogen and hydrogen.

367. The Cyanamide Process

In the early years of the Haber process (1915–1920) it had to compete with the cyanamide process for the production of ammonia. This is accomplished in three steps:

1. Limestone is reduced by coke in an electric furnace:

Equation 8(*a*):

$$CaCO_3 + 4C \rightarrow \underset{\text{Calcium carbide}}{CaC_2} + 3CO$$

2. The calcium carbide is then heated to a white heat (about 800°), and nitrogen (from liquid air) is passed over it.

Equation 8(*b*): $$CaC_2 + N_2 \rightarrow \underset{\text{Calcium cyanamide}}{CaNCN} + C$$

(Ex. 8.)

3. The calcium cyanamide is then treated in autoclaves (§ 153) by high-pressure steam:

Equation 8(*c*): $CaNCN + 3H_2O \rightarrow CaCO_3 + 2NH_3\uparrow$

This process is still used to some extent in the production of ammonia, but is now more important in a modified form, for the production of *calcium cyanide*, § 450.

Calcium cyanamide, when treated with acids, yields *cyanamide* H_2NCN. This, treated with steam, yields *urea*, $CO(NH_2)_2$, which has important industrial uses of its own (§ 451.) (Ex. 9.)

368. Reactions in Liquid Ammonia

As a *solvent*, liquid ammonia is remarkable for its ability to dissolve metallic sodium and other alkali and alkaline-earth metals. Concentrated solutions of these metals in liquid ammonia are usually of a copper-red color, with a bronze metallic luster. More dilute solutions

are of a deep blue color, with an extraordinary capacity for absorbing light.

When solutions of the metals in liquid ammonia are evaporated in a vacuum, solid residues of bronze luster (ammoniates) are obtained, which are believed to be addition compounds of the metal with ammonia (example, $LiNH_3$). When evaporation takes place on warming such solutions the ammonia reacts with the metal to produce an *amide:*

Equation 9: $$Na + NH_3 \rightarrow \underset{\text{Sodamide}}{NaNH_2} + \tfrac{1}{2}H_2 \uparrow$$

The same type of reaction occurs slowly at room temperature, the blue color or metallic luster of the solution gradually disappearing as the colorless amide is produced.

Liquid ammonia dissolves many organic substances, such as resins, fats, and many proteins, which are insoluble in water. Most nitrates and iodides (even silver iodide) are readily soluble, whereas carbonates and fluorides (even those of the alkali metals) are but slightly soluble. Numerous interesting reactions, carried out in solutions of liquid ammonia, include some that are impossible in aqueous solutions because of different solubility relationships, or because the ions concerned are decomposed by water.

Hundreds of compounds are known whose formulas indicate that they are derived from *ammonia* in the same manner that others are derived from *water.* Examples:

HOH Water	$NaOH$ Sodium hydroxide (an aquo-base)	H_3O^+ Oxonium ion	Al_2O_3 Aluminum oxide	$(HO)_2CO$ Carbonic acid
HNH_2 Ammonia	$NaNH_2$ Sodamide (an ammono-base)	H_4N^+ Ammonium ion	AlN Aluminum nitride	$(H_2N)_2C{=}NH$ Guanidine

369. Ammonium Salts

Ammonium sulfate is the source of other ammonium salts, and is used as a fertilizer.

Ammonium chloride (sal ammoniac) is used in dry cells (§ 513). More than ten million cells have been produced in a single year in the United States alone. It is also commonly applied to metal surfaces in soldering. Its usefulness for this purpose depends on its partial dissociation by heat into ammonia and hydrogen chloride, which clean the metallic surfaces to which the solder is to be applied, by reducing or dissolving oxides that may be present.

Ammonium nitrate, mixed with one-fourth its own weight of TNT (§ 381) to serve as a detonator, is a powerful explosive. Dynamite is now often composed of ammonium nitrate, in association with nitrocellulose (§§ 381, 467). It is interesting to notice that ammonium nitrate decomposes in three different ways, according to conditions. Gentle heating yields nitrous oxide and water vapor (§ 373); rapid heating or severe mechanical shock may cause explosive decomposition, yielding nitrogen, nitric oxide, and water vapor; *detonation* with a *fulminating cap*, used in exploding dynamite, yields nitrogen, oxygen, and water vapor. (Ex. 10.)

Ammonium bicarbonate, NH_4HCO_3, is used in baking crackers, since at oven temperatures it is decomposed into gaseous products which render the dough porous.

Calcium ammonium phosphate, $Ca(NH_4)_4(PO_4)_2$, produced by the direct addition of ammonia to superphosphate (§ 388), is now an important fertilizer.

When ammonium salts are strongly heated they are partially dissociated, the usual products being *ammonia gas* and *an acid* (which may itself be decomposed into a non-metallic oxide and water).

$$NH_4Cl + 41.9 \text{ kilocalories} \underset{\text{Recombination}}{\overset{\text{Dissociation}}{\rightleftharpoons}} NH_3 + HCl$$

The fact that heat disappears in this reaction indicates that the dissociation becomes more and more nearly complete the higher the temperature (Van't Hoff's Principle, § 346). This is nevertheless not a practical method for preparing ammonia gas from ammonium salts unless the acid produced is non-volatile, for a volatile acid passes over into the receiver along with the ammonia, where the two recombine.

370. Hydrazine

Hydrazine is a colorless, *very poisonous* liquid, boiling at 113.5°C. Its electronic formula,

$$\begin{array}{c} \quad \ddot{} \;\; \ddot{} \\ H:N:N:H \\ \quad \ddot{H} \;\; \ddot{H} \end{array}$$

indicates that its chemical properties should be similar to those of ammonia but perhaps more pronounced, owing to the fact that it possesses two unshared pairs of electrons instead of one. It is a *vigorous reducing agent*, being easily oxidized to nitrogen or ammonia, or occasionally to hydrazoic acid, HN_3.

Hydrazine also resembles ammonia *in combining directly with acids.* Thus with sulfuric acid it forms hydrazine sulfate, $N_2H_6SO_4$, a white crystalline salt, readily soluble in water. (Ex. 11.)

Hydrazine itself is usually prepared by the action of an excess of dilute ammonium hydroxide on a hypochlorite solution, in the presence of a trace of gelatin. The reaction takes place in two stages:

Equation 10(*a*): $NH_3 + ClO^- \rightarrow \underset{\text{Monochloramine}}{NH_2Cl} + OH^-$

Equation 10(*b*): $NH_2Cl + 2NH_3 \rightarrow \underset{\text{Hydrazine}}{N_2H_4} + NH_4Cl$

371. Hydrazoic Acid and Hydroxylamine

Hydrazoic acid or *azoimide*, HN_3, illustrates the ability of nitrogen, under special circumstances, to form chains of atoms. Recent work has shown that it has the formula $H—N{=}N\rightleftarrows N$, with the three nitrogen atoms in a straight line, in space. It is about as active as acetic acid, and behaves in much the same manner as dilute nitric acid, when treated with vigorous reducing agents. The acid itself and its salts (the *azides*) are unstable, and the heavy-metal azides are violently explosive. Lead azide is used as a detonator for explosives. (Ex. 12.)

Hydroxylamine, NH_2OH, is an unstable base, which is one of the products formed in reducing dilute nitric acid with tin. It is a white solid, which reacts with many different acids to form salts. (Ex. 13.)

372. The Nitrogen Halides

When fluorine is liberated by electrolysis, in the presence of an ammonium salt, a mixture of several different gases is obtained, including *nitrogen trifluoride*, NF_3. This is stable, presumably on account of the small radius of the fluorine atoms and their consequent close approach to the nitrogen atom. We may place this in contrast with *nitrogen trichloride*, NCl_3, which is produced by the action of an excess of chlorine on ammonium hydroxide and is treacherously unstable, exploding at a touch or on being slightly warmed. *Nitrogen triiodide* appears to have the formula NH_3NI_3. It is a brown solid, stable when moist, but when dry explodes violently with a breath of air or the touch of a feather.

373. Nitrous Oxide

Nitrous oxide, N_2O, is easily prepared:

1. By reducing nitric oxide, NO, with moist iron filings. This is the method by which it was first made by Priestley, in 1774. Nitrous

oxide is fairly soluble in cold water, hence in lecture experiments is collected over warm water or a saturated salt solution.

2. By heating solid ammonium nitrate to about 250°C:

Equation 11: $NH_4^+ + NO_3^- \rightarrow N_2O\uparrow + 2H_2O$

Compare this with the result of heating an ammonium salt with a *nitrite*, § 361.

3. Most conveniently, by passing nitric oxide, NO, into a sulfite solution. Direct addition takes place; then on warming the solution the sulfite is oxidized to sulfate and the nitric oxide is reduced to nitrous oxide.

Nitrous oxide readily parts with its oxygen, as is suggested by its structural formula, $N{\equiv}N{\rightarrow}O$. It will therefore support the combustion of phosphorus, carbon, and many other elements, and will cause a glowing splint to burst into flame, as oxygen does. It is easily liquefied by pressure, and is used ("laughing gas") in surgery and dentistry, in admixture with oxygen, for anesthesia.

374. Nitric Oxide

Nitric oxide, NO, is a colorless gas, with the electronic formula $:\dot{N}::\dot{\underset{\cdot}{O}}:$. It will support the combustion of phosphorus, but not of less vigorously burning substances.

The unpaired electron on the nitrogen atom causes nitric oxide to combine directly with a great many other substances; for example, (1) with the oxygen of the air to form nitrogen dioxide, NO_2, and (2) with ferrous ion to form the complex ion $FeNO^{++}$. This ion, in aqueous solutions, happens to be of a dark brown color. It affords a delicate test for nitrates or nitric acid (details in § 382).

Nitric oxide is usually prepared by reducing nitric acid, density about 1.2, with one of the less active metals, such as copper or silver.

375. Nitrogen Dioxide

Nitrogen dioxide is a mixture of two gases, in equilibrium:

Equation 12: $$\underset{\text{Dark brown}}{2NO_2} \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \underset{\text{Colorless}}{N_2O_4}$$

The left-to-right reaction (*a*) liberates heat. The reader should pause to consider (§ 346) whether an increase in temperature will favor reaction (*a*) or reaction (*b*) and so whether it will intensify or diminish the brown color, due to NO_2. (Ex. 14.)

At high temperatures the dioxide is further dissociated, yielding nitric oxide and free oxygen.

Nitrogen dioxide is readily prepared (1) by direct union of nitric oxide with the oxygen of the air, or (2) by reducing concentrated nitric acid with mild reducing agents. It is a vigorous oxidizing agent and thus serves as an oxygen carrier in the manufacture of sulfuric acid in the chamber process (§ 316). It is sometimes used in bleaching flour, since it oxidizes and destroys certain colored impurities that unbleached flour always contains.

376. Nitrogen Pentoxide

When concentrated nitric acid is treated with phosphorus pentoxide (a strong dehydrating agent) and the mixture is distilled under reduced pressure the product is nitrogen pentoxide, a volatile white solid:

Equation 13: $$2HNO_3 + P_2O_5 \rightarrow \underset{\text{Meta-phosphoric acid}}{2HPO_3} + \underset{\text{Nitrogen pentoxide}}{N_2O_5 \uparrow}$$

The oxides of nitrogen, in the gaseous state, are all unusual in that heat is liberated instead of disappearing when they are decomposed into gaseous oxygen and nitrogen. This indicates that they are all essentially unstable. The reason is not far to seek: In separating the atoms that compose the oxide, thus obtaining monatomic nitrogen and oxygen, energy needs to be expended in overcoming the attractive forces, hence heat disappears; but the atoms thus obtained combine in pairs to form molecules, $N \equiv N$ and $O \overset{\cdots}{-} O$ (§ 356), with so great a decrease in potential energy, set free as heat, that this more than offsets the disappearance of heat in the first process.

377. Nitrous Acid and the Nitrites

Nitrous acid is an unstable, moderately active acid. It is largely dissociated, even in dilute solutions, into *nitrogen trioxide*, and this in turn into nitrogen dioxide and nitric oxide:

Equation 14: $$\begin{aligned} 2HNO_2 &\rightleftharpoons N_2O_3 + H_2O \\ &\quad\ \ \rightleftharpoons NO_2 + NO \end{aligned}$$

Nitrous acid may also decompose to give nitric acid and nitric oxide:

Equation 15: $$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$$

All the products indicated in these two equations are obtained whenever an acid is added to a solution of a nitrite.

In the presence of vigorous reducing agents, nitrous acid acts as an *oxidizing agent*, and is itself reduced to nitric oxide, NO; in the presence of vigorous oxidizing agents it serves as a *reducing agent* and is itself oxidized to nitric acid. An explanation has already been given (§ 263). (Ex. 15.)

Nitrous acid (produced as needed by acidifying a solution of a soluble nitrite) is a reagent in the synthesis of many important organic compounds, including dyestuffs, medicinals, and perfumes. *Nitrites* are usually prepared by heating metallic lead with sodium nitrate (about 420°C):

Equation 16: $$NaNO_3 + Pb \rightarrow NaNO_2 + PbO$$

A part of the sodium nitrate is directly converted to sodium nitrite, in this process, by loss of gaseous oxygen.

378. Nitric Acid

Nitric acid is a colorless liquid of density 1.502, boiling at 86°C, with partial decomposition (into NO_2, O_2, and H_2O). It has the formula $\mathrm{H{-}O{-}N}\begin{smallmatrix} \diagup \mathrm{O} \\ \diagdown\!\!\diagdown \mathrm{O}\end{smallmatrix}$. (Ex. 16.)

When diluted with water, nitric acid transfers protons to the water, thus forming the ions H_3O^+ and NO_3^-. Clear proof of this is found in a complete change in the *absorption spectrum* (p. 433), from one in which the $—NO_2$ group is revealed to one having the characteristics of solutions of nitrate salts. Even in dilute solutions nitric acid is still conspicuously an oxidizing agent; otherwise its properties are those of a typical active acid (§§ 185, 191).

379. Preparation of Nitric Acid

1. As a *lecture experiment*, by distilling crystals of sodium nitrate with concentrated sulfuric acid, in a glass retort. The solid residue left in the flask is sodium acid sulfate, $NaHSO_4$, often called "niter cake." The same process is responsible for about half of the nitric acid used in industry. Cast-iron retorts are employed, and distillation is carried out under reduced pressure, to lower the temperature at which the acid distils, and thus reduce loss of the acid by decomposition. (Ex. 17.)

2. Nitric acid is produced on a large scale by the oxidation of ammonia gas by atmospheric oxygen, in the presence of a catalyst

of finely divided platinum. In the first stage of the reaction nitric oxide is produced:

Equation 17: $$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

The nitric oxide, in the presence of water and more oxygen, is converted to nitrogen dioxide, NO_2, and finally into nitric acid:

Equation 18: $$4NO + 3O_2 + 2H_2O \rightarrow 4HNO_3$$

380. Nitric Acid as an Oxidant

When it serves as an oxidant, nitric acid is reduced to compounds representing one or more of the lower valence states of nitrogen:

$$\begin{array}{l}\text{Valence state:} \quad \overset{+5}{HNO_3} \rightarrow \overset{+4}{N_2O_4} \rightarrow \overset{+3}{N_2O_3} \rightarrow \overset{+2}{NO} \rightarrow \overset{+1}{N_2O} \rightarrow \overset{0}{N_2} \rightarrow \overset{-1}{NH_2OH} \rightarrow \overset{-2}{N_2H_4} \rightarrow \overset{-3}{NH_3}\end{array}$$

We shall give three examples:

1. The more vigorous the reductant used, and the more dilute the nitric acid the greater the probability is that all these stages of reduction will be passed through and *ammonia* appear as the final product. This happens when nitric acid or a nitrate, in dilute solution, is treated with zinc and sulfuric acid, or zinc and sodium hydroxide:

Equation 19: $$HNO_3 + 8H^+ + 4Zn \rightarrow 4Zn^{++} + NH_3\uparrow + 3H_2O$$

As a valence state equation this would be written:

Equation 19(*a*): $$N^{+5} + 4Zn^0 \rightarrow N^{-3} + 4Zn^{++}$$

(Check by counting electrical charges: net, +5, on each side.) The addition of a few drops of a solution of some cupric salt will cause metallic copper to be deposited on the zinc and hasten the reaction, by forming a *couple* (§ 516).

2. Nitric acid, diluted with about its own volume of water, is reduced by the less vigorous reductants, such as metallic copper, to form *nitric oxide*. The reaction begins very slowly, but soon becomes vigorous, since it is self-catalyzed by small amounts of nitrogen dioxide, NO_2, that are set free. If we disregard intermediate steps (the real oxidizing agent being nitrogen dioxide) the reaction may be written

Loss, 3 units

No change

$$Cu + HNO_3 + HNO_3 \rightarrow Cu(\check{N}O_3)_2 + \check{N}O + H_2O \text{ (unbalanced)}$$

Gain, 2 units

We have written HNO_3 twice on the left-hand side of the equation, as a preliminary to balancing, since nitrogen appears in two different compounds, with two different valence numbers, on the right-hand side.

By taking account of the changes in valence number that occur (a gain of 2 for Cu, and a loss of 3 for N) we see that to make loss equal gain we must write 3Cu and $2HNO_3$ on the left-hand side of the equation, hence $3Cu(NO_3)_2$ and 2NO on the right-hand side. But the 6 nitrate groups in $3Cu(NO_3)_2$, on the right, will call for $6HNO_3$ on the left, in addition to the $2HNO_3$ already indicated for the production of nitric oxide. We then have a total of 8 hydrogen atoms on the left, hence must write $4H_2O$ on the right. The balanced equation is therefore:

Equation 20: $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

As a final check, count oxygen atoms: 24 on each side of the equation.

3. With concentrated nitric acid and slightly active metals, such as copper or silver, the nitric acid is chiefly reduced to nitrogen dioxide, NO_2:

$$Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O \text{ (unbalanced)}$$

This is left for the student to balance, according to the model just given. (Ex. 18.)

381. Uses of Nitric Acid

About three fourths of the nitric acid now made is used (even in times of peace) in the *manufacture of explosives*. These are of three chief types:

1. Nitroglycerin is prepared by the action of nitric acid on glycerol (technically called glycerin):

$$\underset{\text{Glycerol}}{C_3H_5(OH)_3} + 3HNO_3 \rightarrow \underset{\text{Glycerol trinitrate}}{C_3H_5(ONO_2)_3} + 3H_2O$$

The product, glycerol trinitrate, is technically called *nitroglycerin*.

Dynamite consists of nitroglycerin absorbed in a porous material, such as wood flour, with or without admixture of nitrocellulose or ammonium nitrate. Its chief uses are in clearing land, quarrying rock, mining coal, and executing such engineering feats as the Panama Canal or railroad tunnels through mountain ranges. Before the invention of dynamite such construction work proceeded hardly more rapidly than was possible in the days of the Roman Empire, when slaves drilled tunnels by attacking the face of the rock with a suspended, swinging wooden ram, shod with an iron beak.

2. *Nitrocellulose explosives* are made by the action of the mixture of nitric and sulfuric acids on purified wood pulp or cotton linters, both of which are nearly pure cellulose—an organic hydroxy compound. Details are given in § 467.

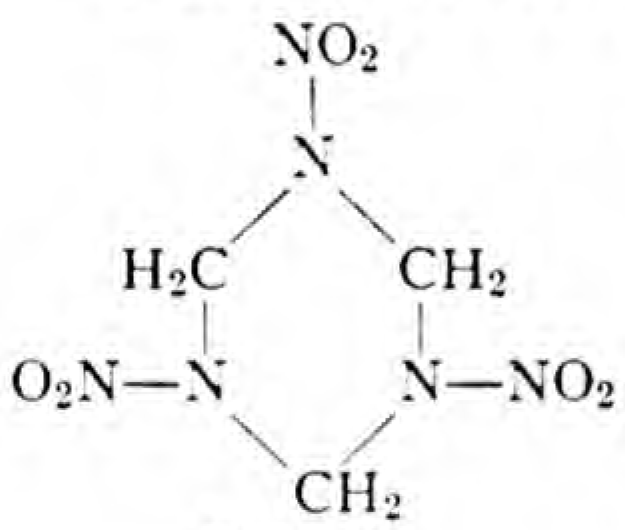
3. *High explosives* are made by the action of nitric acid on phenol and other substances of the *aromatic* group; one or more hydrogen atoms of the aromatic substance are replaced by nitro groups, $—NO_2$. For example:

$$\underset{\text{Phenol}}{C_6H_5OH} + 3HNO_3 \rightarrow \underset{\substack{\text{Trinitrophenol}\\\text{(picric acid)}}}{C_6H_2OH(NO_2)_3} + 3H_2O$$

By a similar reaction, toluene, a close relative of phenol (§ 463), is converted into trinitrotoluene (TNT).

$$\underset{\text{Toluene}}{C_6H_5(CH_3)} + 3HNO_3 \rightarrow \underset{\text{TNT}}{C_6H_2(CH_3)(NO_2)_3} + 3H_2O$$

During the recent war a new group of high explosives were developed, which until recently remained secret. One of these is *cyclonite*, which is produced by nitration of hexamethylenetetramine. Its particularly violent explosive properties appear to be due to the fact that it contains nitrogen linked to nitrogen, instead of the nitrogen-to-carbon linkage of most other high explosives.



Cyclonite

Observe that glycerol trinitrate (nitroglycerin) and guncotton are true nitrates, containing the *nitrate* group, $—ONO_2$, with nitrogen linked only to oxygen. High explosives, on the contrary, contain the *nitro group*, $—NO_2$, with nitrogen linked to carbon.

Both classes of explosives are set off by a *detonator*. Oxygen yielded by the nitro or nitrate groups combines with the carbon and hydrogen of the explosive to form carbon monoxide, carbon dioxide, and water vapor, while the nitrogen atoms combine in pairs, according to their familiar habit, forming free nitrogen. The tremendous outrush of gases thus liberated is made the more violent by the expansion caused by the great quantity of heat set free in the reaction. All this has happened, and the explosion is done with and over, before the sound that it creates in rending the earth and atmosphere has traveled more than a few feet.

By treating cellulose with a somewhat diluted mixture of nitric and sulfuric acids for a shorter time than is required in the production of guncotton, we obtain a material called *pyroxylin*, which is used in the production of plastics and lacquers (§ 467). This use accounts for about 15 per cent of the nitric acid now consumed in industry.

The remaining 10 per cent of the nitric acid used in industry goes into the production of *organic nitrates* and various *nitro derivatives* (§ 463) which serve as *intermediates* in the manufacture of dyestuffs, medicinals, and perfumes. (Ex. 19.)

382. Tests for Nitrogen

1. *Elementary nitrogen* is best distinguished from other inert gases, such as argon, by its ability to combine with magnesium and a few other active metals, when a slow current of the gas is passed over the heated metal. The *nitrides* thus formed, Mg_3N_2, Li_3N, etc., are hydrolyzed by water, yielding ammonia, which is recognized as next described.

2. *Ammonium salts*, in any considerable concentration, are easily detected by warming the solution with an alkali, thus expelling *ammonia gas*, which may readily be recognized by its odor or by its ability to turn moist red litmus blue.

The presence of traces of ammonia or ammonium salts in water may be detected by the addition of *Nessler's solution*.[1] A yellow to orange-yellow coloration (due to a complex salt, $NH_2Hg_2I_3$) is present when as little ammonia is present as one part in ten million. Large quantities of ammonia produce a yellow-brown precipitate, unless precipitation is prevented by the addition of gelatin (about $\frac{1}{4}$ per cent).

3. *Combined nitrogen* in foodstuffs or in many other organic materials may be determined by the famous *Kjeldahl method*. A small sample of the material is boiled with concentrated sulfuric acid and (often) a catalyst (a crystal of copper sulfate or a trace of selenium) in a round-bottomed flask, until all the organic matter has been oxidized and destroyed. The nitrogen of the organic matter is then present in solution as an ammonium salt. When the solution has cooled it is attached to a condenser, treated with an excess of alkali, and boiled until the ammonia set free has been driven over into a measured volume of a standard acid. *By determining the amount of*

[1] Nessler's solution is prepared by adding an iodide to a solution of a mercuric salt, in sufficient quantity nearly but not quite to redissolve the precipitate that is at first produced. The solution then contains the complex salt, K_2HgI_4.

acid which this ammonia neutralizes we may calculate how much nitrogen was present in the original sample.

4. *Nitrites*, when a dilute solution is made faintly acid with acetic acid, yield nitric oxide and nitrogen dioxide, recognizable by a deep brown color (the ion $FeNO^{++}$) produced with solutions of a ferrous salt. Nitrites are also sometimes recognized by the evolution of gas (CO_2 and N_2), when urea is added to an acidified solution.

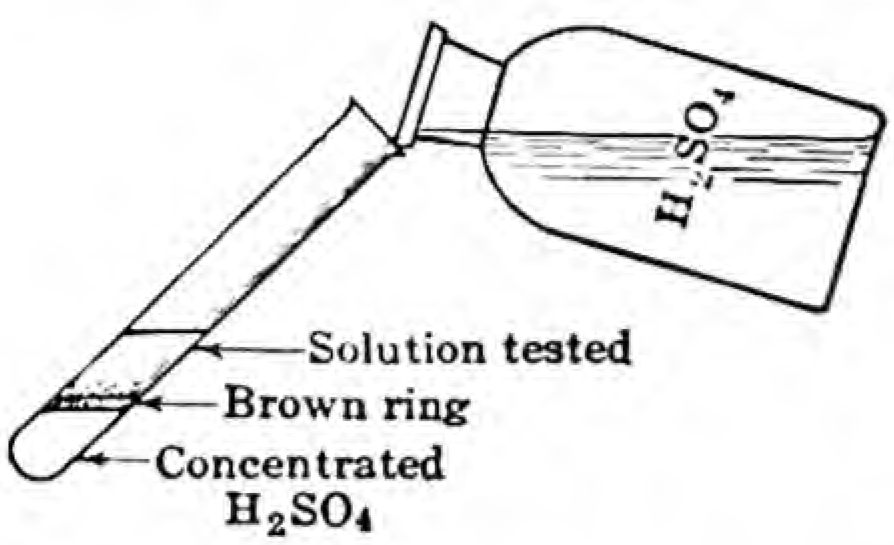


FIG. 126. The brown ring test for nitrates.

5. *Nitrates* respond to the ferrous salt test for nitrites, except that the activity of the acid added must be greatly increased, as by using sulfuric acid, which is layered beneath the solution to be tested, containing a little ferrous salt (Fig. 126). Iodides yield a similar color, which beginners often mistake for the test for a nitrite or nitrate.

6. A better test for *nitrates* consists in adding about 1 ml of concentrated sulfuric acid to an equal volume of the solution to be tested, *in the known absence of nitrites, chlorates, and perchlorates.* Then add a small fragment of bright metallic copper, and warm. In the presence of a nitrate the copper will react, forming a cupric salt (blue solution) and nitrogen dioxide (brown gas). (Ex. 20–28.)

Technical Words

Heat of dissociation—the energy that must be expended in dissociating one mole of a substance into specified products.

Interatomic distance, p. 411.

Nitrogen fixation—any process that brings nitrogen into chemical union with other elements.

In addition to nitrogen fixation by *nitrogen-fixing bacteria* (§ 362) we have nitrogen fixation in the formation of *nitrides*, when magnesium and other metals are heated in an atmosphere of nitrogen (§ 382); the direct union of nitrogen and hydrogen to form *ammonia* in the Haber process (§ 366); the reaction of nitrogen with calcium carbide to form calcium cyanamide (§ 367); and the formation of oxides of nitrogen in lightning flashes or in an electric arc (§ 362).

Ammonifying bacteria—bacteria that bring about the decay of dead animal and plant materials or waste products in the presence of a plentiful supply of atmospheric oxygen, to produce ammonia or ammonium salts.

Nitrifying bacteria—bacteria that oxidize ammonium salts to nitrites, then to nitrates.

Ammonification, nitrification—processes carried out by the groups of bacteria just mentioned.

Denitrification—any process in which fixed or combined nitrogen is returned to the atmosphere as free nitrogen. (Obviously not the reverse of *nitrification*.)

Detonator—an explosive or explosive mixture that is exploded by a shock or a flame from a fuse, and that serves to induce the explosion of another material, itself relatively insensitive to the agencies that set off the detonator. The principal detonators are mercury fulminate, $Hg(ONC)_2$, and lead azide, $Pb(N_3)_2$. Their action is usually rendered less violent by admixture with potassium chlorate and some slow-burning material, such as antimony trisulfide.

Detonation—an explosion characterized by great violence and almost instantaneous propagation throughout the whole mass of the explosive material, as contrasted with the relatively slow propagation of the explosive wave in propellent explosives. In an automotive engine improper fuel results in detonation that is audible as a knock.

Fulminating cap—a cap for ammunition, containing a detonating charge, perhaps including mercury fulminate.

Intermediate—any substance (particularly one of the aromatic group) that is itself the product of chemical manufacture and that serves as raw material in the production of more complicated compounds (dyestuffs, medicinals, perfumes, etc.).

Symbiosis—a relationship in which living organisms of different species live together and benefit from each other.

Flux—any substance added to a reaction mixture in a furnace to induce fusion, either by being itself readily fusible or by reacting to produce readily fusible products.

Absorption spectrum—a spectrum (p. 279) formed by absorption of some of the frequencies of white light, when passed through a transparent medium.

Exercises

1. Write an equation for a reaction in which metallic copper combines with atmospheric oxygen in the presence of ammonium hydroxide, forming the blue solution mentioned in the text.

2. Assuming that air contains 80 mole per cent nitrogen, how many liters of nitrogen are contained in 15 liters of air, and how much additional nitrogen will result when the oxygen in this air reacts with ammonia?

3. What volume of nitrogen under standard conditions will result from the reaction of an excess of ammonium chloride solution with 67 ml of sodium nitrite solution, density 1.03g/ml, containing 5 per cent $NaNO_2$?

4. Give equations for the reactions in which nitrogen is fixed by lightning flashes, then converted into soluble nitrates.

5. When nitrites and ammonium salts are found together in the soil, some denitrification may occur. Explain (§ 361).

6. Show that ammonia acts as a base in the broadest sense when it reacts with water to form ammonium hydroxide.

7. Show how the partial pressures of the three gases concerned in the Haber process enter into the expression for the equilibrium constant (§ 343). The constant, K_p, for this reaction (equation in § 366) is 0.0001 at a certain temperature. Determine what the equilibrium pressure of the nitrogen must be when that of the hydrogen is 3 atmospheres and that of the ammonia is 0.05 atmosphere.

8. Calcium cyanamide is the calcium salt of cyanamide, H_2NCN. Write a

graphic formula (§ 248) for the latter that will give each nitrogen and carbon atom a complete octet.

9. Urea reacts with nitrous acid to form nitrogen, carbon dioxide, and water vapor. Write and balance an equation.

10. Give equations to represent the three different ways in which ammonium nitrate may decompose.

11. Give an electronic formula for the cation in hydrazine sulfate

12. What is the formula of lead azide? What products would you expect to result from its decomposition, when it serves as a detonator?

13. Give an electronic formula for hydroxylamine. Then account for its ability to react with acids to form salts, in much the same manner as ammonia (§ 364, item 3).

14. Predict the effect of heat on the color of nitrogen tetroxide.

15. Write and balance equations for the reactions to be expected when nitrous acid reacts with an iodide, and with hydrogen peroxide, respectively. Indicate whether nitrous acid is an oxidizing or reducing agent in each reaction, and what changes in valence number occur.

16. How many electrons are used in bonding nitrogen to oxygen in nitric acid, if the molecule contains two double bonds? How many, if one of the two double bonds were replaced by a coordinate bond, nitrogen donating a pair of electrons to oxygen?

17. Give an equation for the decomposition of nitric acid by heat, assuming that it is the reverse of a reaction by which nitric acid may be synthesized from gaseous products.

18. When nitric acid oxidizes arsenic trioxide to arsenic acid it is itself reduced to nitrogen trioxide. Write electronic equations, and combine in such proportions that electrons cancel out.

19. What name is given to explosives used to induce the explosion of other materials?

20. What are the three chief classes of explosives? In what radical does the nitrogen occur, in each class?

21. How is dynamite prepared? What sort of chemical change takes place in its explosion?

22. What are the chief uses of nitric acid, other than in the production of explosives?

23. What are the chief industrial uses of the most important ammonium salts?

24. From memory, sketch the cycle of nitrogen in nature, and indicate the manner in which each of its principal stages is accomplished.

25. Distinguish between nitrogen fixation and nitrification.

26. Describe the Kjeldahl test for nitrogen, indicating successive steps, and the purpose of each.

27. Describe tests for elementary nitrogen, ammonium salts, and nitrites, giving equations for the reactions concerned.

28. How may nitrites be distinguished from nitrates? Describe a good test for nitrogen in the form of nitrate.

Chapter 28

THE RELATIVES OF NITROGEN

383. Comparing the Members of the Nitrogen Family

In § 356 we compared nitrogen with oxygen and fluorine, next toward the right of nitrogen in the Periodic Table. We found that differences in properties were very largely accounted for by the existence of a triple bond between the atoms in N_2, a modified double bond in O_2, and a single bond in F_2.

Now let us compare nitrogen with its own nearest relatives, just below it in the same column of the Periodic Table:

Atomic Number	*Electron Groups*	*Symbol*		*Formula*	
7	2,5	N	Nitrogen	N_2	Gas
15	2,8,5	P	Phosphorus	P_4 (vapor)	Yellow or red solid
33	2,8,18,5	As	Arsenic	$As_4 \rightleftharpoons 2As_2$	Gray solid
51	2,8,18,18,5	Sb	Antimony	$Sb_4 \rightleftharpoons 2Sb_2$	Lustrous gray solid
83	2,8,18,32,18,5	Bi	Bismuth	$Bi_2 \rightleftharpoons 2Bi$	Dark gray solid

We observe a rapid alteration of properties, as we pass down the list, a gas giving place to a volatile solid, then less volatile solids, as non-metallic properties are gradually suppressed and metallic properties appear. This progressive alteration in properties is in part caused by increasing atomic radius, which is effective in preventing atoms of phosphorus (or of the elements below phosphorus in the table) from drawing close enough together to establish the triple bond that gives us the molecule N_2.

We notice, furthermore, that the group of electrons next below the valence level of 5 electrons increases from 2 in nitrogen to 8 in phosphorus, and 18 in the other elements of this group. This alteration, in addition to increased atomic radius, greatly weakens the attraction that the positively charged nucleus of the atom can exert upon the out-

lying group of 5 valence electrons. In consequence, antimony has a slight tendency to lose several of its valence electrons (thus functioning as a metal), whereas bismuth fairly readily does this (thus being a typical metal, in all its reactions).

We have just observed a tendency which is displayed not only among the relatives of nitrogen but also in all the neighboring columns (3A to 7A) of the Periodic Table: *In passing down any given column, non-metallic properties give place to metallic properties* (most rapidly in Column 3A, least rapidly in Column 7A), *on account of a weakening of the attraction of the nucleus for the valence electrons, with increased atomic radius and increased number of electrons in next inner group.*

The chief valence states of phosphorus are shown in this table. The same ones (except for +1 and +6) are known for arsenic, antimony, and bismuth:

Valence Number	*Oxide or Hydride*	*Acids*			*Salt*
−3	PH_3 Phosphine				PH_4I Phosphonium iodide
0	P_4				
+1	P_2O	H_3PO_2 Hypophosphorous acid			NaH_2PO_2 Sodium hypophosphite
+3	P_4O_6	H_3PO_3 Orthophosphorous acid	HPO_2 Metaphosphorous acid	$H_4P_2O_5$ Pyrophosphorous acid	Na_2HPO_3 Sodium orthophosphite
		(Salts of these acids are active reducing agents)			
+4	PO_2	$H_4P_2O_6$ Hypophosphoric acid			
+5	P_2O_5	H_3PO_4, HPO_3, $H_4P_2O_7$ (§ 428)			Na_3PO_4 Sodium orthophosphate
+6	PO_3 (unimportant)				

PHOSPHORUS

384. Occurrence of Phosphorus

Phosphorus is quite as necessary to life as nitrogen itself. The bony framework and teeth of vertebrates contain a large proportion of modified calcium phosphate. The brain and nervous tissue contain phos-

phoproteins. Indeed, a minute amount of phosphorus is contained in every cell of every living plant and animal—in the cell-nucleus, the structural element that is most intimately associated with the phenomena of growth and reproduction.

Phosphorus minerals are all salts of orthophosphoric acid, H_3PO_4. Its calcium salt, $Ca_3(PO_4)_2$, is never found pure in nature, nor can it be prepared artificially in crystalline form, presumably because this particular grouping of ions is geometrically difficult, with the ionic radii concerned. By the introduction of a fluoride, chloride, or hydroxyl ion for every three phosphate ions it becomes possible to construct a stable space-lattice (the extra negative charge introduced by the fluoride, chloride, or carbonate ions being offset by the incorporation of extra calcium ions, elsewhere in the crystal lattice). Thus we account for *apatite*, $Ca_5(PO_4)_3F$, already mentioned (§ 269).

By the action of carbonic acid and water, apatite and other phosphate minerals are brought into solution and become available for growing plants. These in their turn hand on the phosphorus to animals. On the ocean bottom in many parts of the world are found *phosphatic nodules*, which consist of calcium phosphate that has been dissolved from the bones and teeth of fish and then redeposited with fluoride or carbonate, around unchanged material.

Limestone beds often contain considerable amounts of phosphate, intermingled with the predominating calcium carbonate. These deposits are often leached by running water, after being uplifted into dry land, leaving phosphatic pebbles or nodules, associated with clay. This is the origin of most deposits of *phosphate rock*—impure calcium phosphate. The chief geographical sources of phosphate rock in the United States are Florida, South Carolina, Tennessee, and the Rocky Mountain states. About half of the world's production comes from Tunis, Algiers, and Morocco, in northern Africa.

385. Elementary Phosphorus

At the present time, phosphorus is commonly prepared in electric furnaces, in which phosphate rock, sand, and powdered coke are heated together at a high temperature:

$$Ca_3(PO_4)_2 + 3SiO_2 \rightarrow 3CaSiO_3 + P_2O_5$$

$$2P_2O_5 + 10C \rightarrow 10CO\uparrow + P_4\uparrow$$

The sand unites with calcium oxide to form calcium metasilicate, $CaSiO_3$; the phosphoric anhydride, P_2O_5, thus set free, is immediately

reduced by the carbon to elementary phosphorus, which distils away through an opening near the top of the furnace, and is condensed in cold water (Fig. 127).

The inability of phosphorus atoms, because of their large radius, to establish triple bonds among themselves results in the phosphorus molecule having a very different structure from the nitrogen molecule.

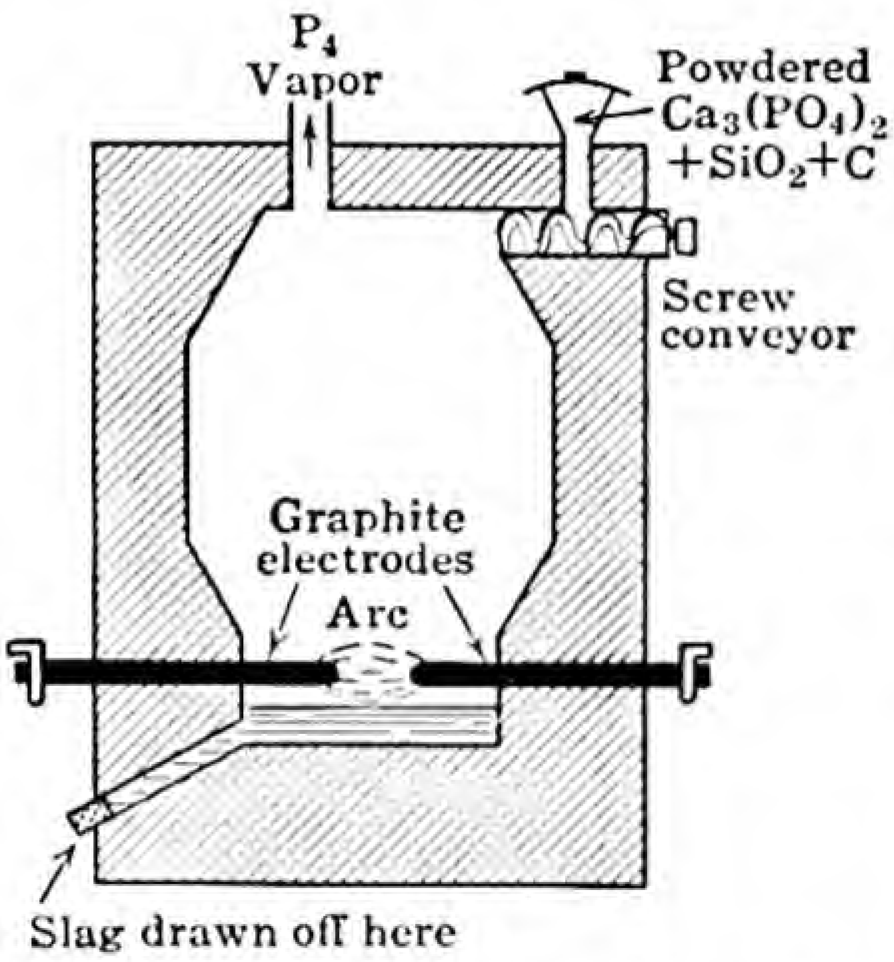


FIG. 127. Production of elementary phosphorus in an electric furnace.

In phosphorus vapor the molecule is a tetrahedron, P_4, with a phosphorus atom in each of the four corners, singly linked to each of its three neighbors. This is a relatively weak structure, readily broken down by the attack of any active agent, such as oxygen. That is why phosphorus vapor is so flammable.

In solid *white phosphorus* (usually yellowish on the surface) the P_4 groups are packed into a hexagonal structure, each group being protected against external reagents by the presence of its neighbors, hence tendency toward oxidation is reduced, in comparison with phosphorus vapor. This is the ordinary form of phosphorus. It is extremely poisonous, readily soluble in carbon disulfide, and so flammable that it will catch fire from the heat generated by its slow oxidation when exposed to the air. It must never be touched with the fingers; it must be preserved and cut up under water or under a solution of copper sulfate (which will gradually cover the sticks of phosphorus with a protective coating of metallic copper).

Red phosphorus is most conveniently obtained by heating the white (yellow) form with a trace of iodine, which catalyzes the transformation. It is stable, practically non-poisonous, insoluble in solvents for the yellow form, and ignites only when strongly heated. By being distilled it may be reconverted into the white form. Both forms give the same product when burned in the air. The atoms in the red form have been crowded together into a cubic structure, each atom tending to share a pair of electrons with four nearest neighbors, but some electrons remaining unshared. The result is a solid of somewhat variable physical properties, which is perhaps best viewed as a solid solution of white phosphorus in a dense, faintly conductive form called *black*

phosphorus (obtainable by heating white phosphorus to a high temperature under high pressures).

An interesting reaction is observed when a very small fragment of phosphorus is gently boiled with a dilute alkali, in a flask fitted with a tube to deliver the gaseous product under the surface of a dish of water (Fig. 128). The gaseous product is *phosphine* (poisonous):

$$P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{Phosphine}}{PH_3\uparrow} + \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2}$$

As the phosphine enters the air it catches fire, burning to form smoke rings of metaphosphoric acid, HPO_3.

Phosphine is evidently analogous to ammonia, NH_3. Phosphonium salts, corresponding to ammonium salts, are also known.

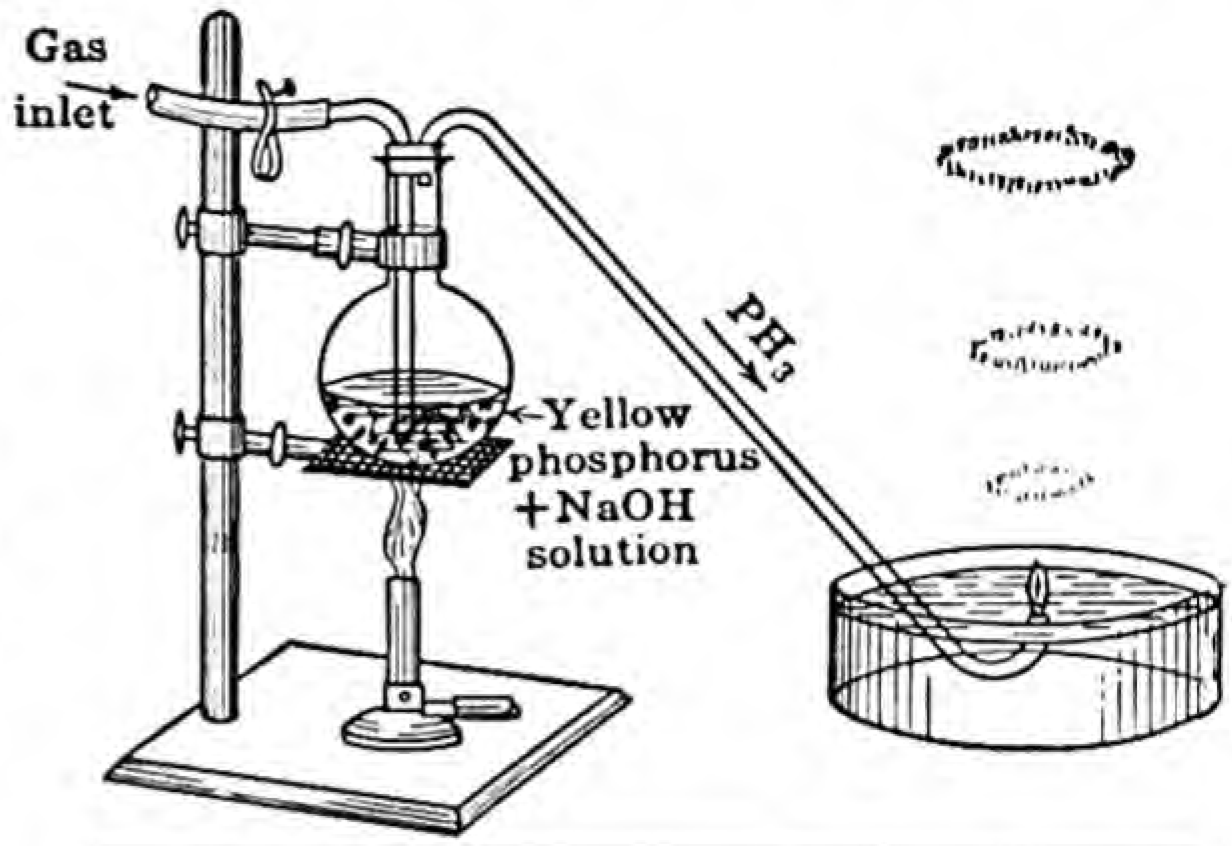


FIG. 128. Preparation of phosphine as a lecture experiment. Before heating the mixture in the flask it is necessary to displace air from the apparatus by introducing illuminating gas through the gas inlet shown at the left.

386. Matches

The chief use of elementary phosphorus is in the match industry. In former years, yellow phosphorus was used; but workmen suffered so seriously from chronic phosphorus poisoning that such matches were taxed out of existence. At the present time, only red phosphorus and phosphorus trisulfide, P_4S_3, are used.

In a "*strike anywhere*" *match* the head is tipped with a mixture that is chiefly phosphorus trisulfide, P_4S_3, which is readily ignited by the heat of friction. The main portion of the head is a mixture of combustible material, such as sulfur, rosin, or antimony trisulfide, with oxidizing agents such as lead dioxide and potassium chlorate, and glue to serve as a binder. The stick is usually coated with paraffin and impregnated with ammonium phosphate, which prevents the stick from continuing to glow after the match has been extinguished. (Ex. 1, 2.)

In the *safety match* the material in the head is sulfur or antimony trisulfide, Sb_2S_3, with a little potassium chlorate or potassium dichromate to serve as an oxidizing agent, powdered glass to increase the fric-

tion, and some glue to hold the mass together. This mixture is not combustible enough to be ignited easily, unless struck upon a box coated with red phosphorus, which is vaporized and the vapor ignited by the heat generated by friction in striking the match against the box.

387. The Three Phosphoric Acids

Phosphorus pentoxide, P_2O_5, is an effective drying agent for gases, on a laboratory scale. It may combine with water in three different stages:

$$P_2O_5 + H_2O \rightarrow \underset{\text{Metaphosphoric acid}}{2HPO_3}$$

$$P_2O_5 + 2H_2O \rightarrow \underset{\text{Pyrophosphoric acid}}{H_4P_2O_7}$$

$$P_2O_5 + 3H_2O \rightarrow \underset{\text{Orthophosphoric acid}}{2H_3PO_4}$$

The prefix *ortho-*, in inorganic chemistry,[1] refers to an acid which by loss of water may be converted into a *pyro*-acid; and this, sometimes, by loss of more water, into a *meta*-acid. Metaphosphoric acid is usually produced when phosphorus pentoxide is added to cold water; and orthophosphoric acid when the solution is boiled, or upon standing for several days.

The ability of phosphorus to form three different acids, whereas nitrogen, in the same valence number (+5), forms only HNO_3, is a consequence of the larger atomic radius of phosphorus, which enables it to make contact with (coordinate) four different oxygen atoms at once, instead of only three. (Ex. 3, 4.)

Orthophosphoric acid (generally called *phosphoric acid*, without any qualifying prefix) is now usually made by heating phosphate rock with sand and coke in an electric furnace. The phosphorus thus produced (§ 385) is burned to form phosphorus pentoxide, which is absorbed in water to form phosphoric acid. This forms *normal phosphates* (*e.g.*, Na_3PO_4), in which all three of the hydrogen atoms in each molecule of acid are replaced by metals; and *acid phosphates* (*e.g.*, Na_2HPO_4 and NaH_2PO_4), in which one or two hydrogen atoms remain unreplaced. (Ex. 5, 6.)

X-ray research has revealed that the phosphate ion is practically a regular tetrahedron, with a phosphorus atom at the center, and four oxygen atoms distributed nearly symmetrically about it, at distances

[1] In organic chemistry the prefixes *ortho-* and *meta-* have other meanings (§ 462).

from each other of 2.46 to 2.60 Å. In the crystalline acid phosphates, such as KH_2PO_4, the phosphate tetrahedra are linked through hydrogen bonds (§ 272) to form a network, with cations fitted into the meshes, according to a regular space pattern.

388. Phosphate Fertilizers

Finely ground phosphate rock is often used directly as a fertilizer. It is practically insoluble in pure water, but is gradually brought into solution by slightly active acids in the soil. A plant with a vigorous and freely branching root system, such as that possessed by Indian corn, can make better use of phosphate rock than a plant lacking that advantage.

If ground phosphate rock is treated with a limited amount of sulfuric acid of 50 to 60 per cent strength, a vigorous reaction takes place, with the liberation of a considerable amount of heat. The crystal structure of the phosphate rock is broken down, and its fluoride component (§ 384) is expelled as hydrogen fluoride. The result is a highly acid, pasty mass, which contains monocalcium phosphate, $CaH_4(PO_4)_2$, mixed with calcium sulfate. This mixture is called *superphosphate.* (Ex. 7.)

In the presence of siliceous impurities even superheated steam will expel hydrogen fluoride from phosphate rock (an important recent discovery, which may deprive sulfuric acid of one of its important uses).

By either method we obtain monocalcium phosphate, which is readily soluble. When this is applied to the soil it reacts with the limestone particles there present to form dicalcium phosphate, $Ca_2H_2(PO_4)_2$, often called *reverted phosphate.* This is more readily available to growing plants than the original phosphate rock because it is extremely finely subdivided, in consequence of being formed by precipitation about the limestone particles of the soil.

389. Test for Phosphorus

Small amounts of phosphorus in organic matter (in foodstuffs, for example) are best detected by oxidizing the material with nitric acid, thus securing a solution of (ortho)phosphoric acid. Phosphate fertilizers need only be extracted with water or dilute acids. To the phosphoric acid solution thus obtained (containing nitric acid) there is added a considerable quantity of ammonium nitrate. Then a solution of ammonium molybdate (a substance of variable formula) is added, and the solution is warmed. A yellow precipitate is formed, ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$.

ARSENIC

390. Occurrence of Arsenic

Arsenic occurs in nature in combination with many metals, as well as with sulfur. Arsenical pyrites (mispickel, FeAsS) is the most important mineral.

During the roasting of sulfide ores containing arsenic the arsenic is oxidized to arsenic trioxide, As_2O_3, which sublimes and collects as dust in the flues. From this the element itself may be prepared by reduction with carbon.

Arsenic, like sulfur and phosphorus, occurs in several distinct forms. The most common of these is a crystalline, steel-gray substance, with a bright metallic luster.

All the soluble arsenic compounds are extremely poisonous.

391. Compounds of Arsenic

The most important arsenic compound is *arsenic trioxide*, As_2O_3. This is a white solid, formed by burning elementary arsenic in the air. It is popularly called "arsenic" or "white arsenic." It is not very soluble in water, but dissolves readily in dilute alkalies or alkali carbonates to form soluble *arsenites:*

$$As_2O_3 + 2OH^- \rightarrow \underset{\text{Metarsenite ion}}{2AsO_2^-} + H_2O$$

$$As_2O_3 + CO_3^{--} \rightarrow 2AsO_2^- + CO_2\uparrow$$

Arsenites are vigorous reducing agents. When they act as reducing agents they are themselves oxidized to arsenates.

Arsenic trioxide also dissolves readily in hydrochloric acid, forming arsenic trichloride, $AsCl_3$, a typical covalent compound, which volatilizes when solutions containing it are heated. It is *extremely poisonous.* Arsenic trichloride, like non-metallic halides in general, is completely decomposed by reaction with water.

$$AsCl_3 + 2H_2O \rightarrow \underset{\substack{\text{Metarsenious}\\ \text{acid}}}{HAsO_2} + 3HCl$$

(Ex. 8–12.)

Arsenic pentoxide, As_2O_5, is likewise a white solid. Its behavior is similar to that of arsenic trioxide; that is, it reacts with solutions of alkalies and alkali carbonates to form *arsenates*, *i.e.*, the orthoarsenate ion, AsO_4^{---}. It reacts with concentrated hydrochloric acid to form arsenic pentachloride, $AsCl_5$. This is hydrolyzed by water to form arsenic acid, H_3AsO_4.

Arsenates are converted into arsenites by many reducing agents. The most vigorous reducing agents, however, produce arsine, AsH_3, an extremely poisonous gas, in which the valence number of arsenic is -3. (Ex. 13, 14.)

392. Uses of Arsenic and Its Compounds

Arsenic is added to lead to harden it, in making shot, and to brass and other alloys to improve their strength and casting qualities. Arsenic improves the resistance of cast iron to oxidation (grates and fire-boxes). Arsenic trioxide is a component of many kinds of fusible glass and decorative white enamels.

Most of the other industrial uses of arsenic compounds depend on their poisonous properties. Calcium arsenate has been widely used in combating the boll weevil that has so seriously threatened the cotton industry of the South. The fields are often dusted with calcium arsenate from airplanes. Other important preparations used in combating leaf-devouring insects are: Paris green, which is copper arsenite-acetate, $Cu_3(AsO_3)_2 \cdot Cu(C_2H_3O_2)_2$; lead arsenate, $Pb_3(AsO_4)_2$; and solutions of sodium metarsenite, $NaAsO_2$. These are often mixed with bran and molasses before being applied to the fields. (Ex. 15, 16.)

393. Tests for Arsenic

1. Both arsenites and arsenates give a yellow precipitate, consisting largely of arsenic trisulfide, when hydrogen sulfide is passed into a hot solution, strongly acidified with hydrochloric acid. An arsenate is precipitated only very slowly, since it takes time to effect the reduction to the trivalent condition.

2. Arsenates give a chocolate-brown precipitate of silver orthoarsenate, Ag_3AsO_4, with silver nitrate solution.

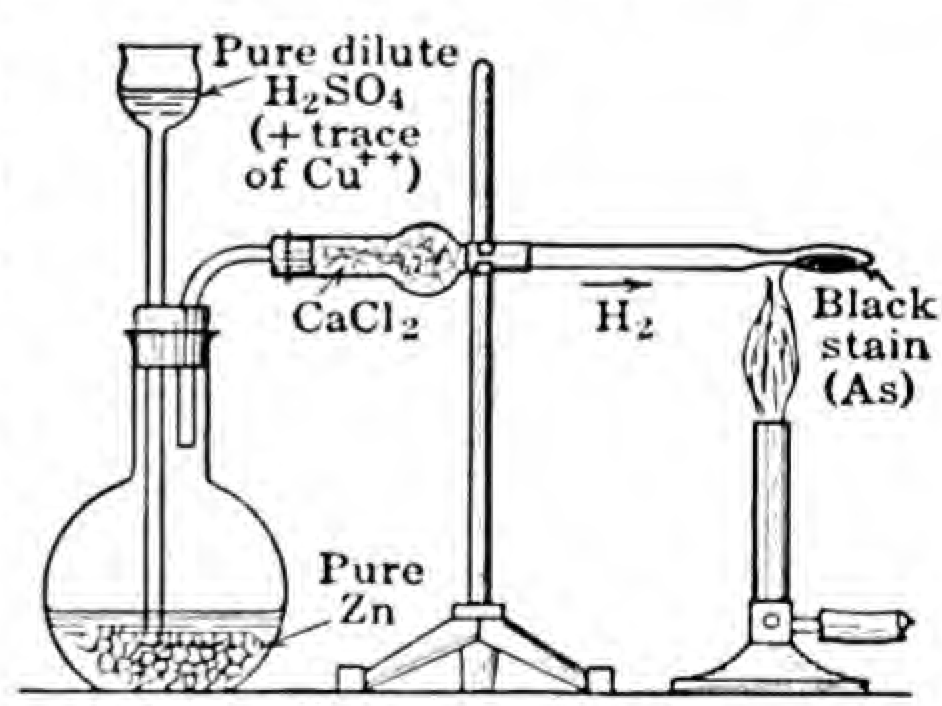


FIG. 129. The Marsh test for arsenic.

3. A delicate test for arsenic is the *Marsh test* (Fig. 129). This depends on the reduction of the arsenic, by treatment with zinc and an acid, the final product being arsine.

$$\underset{\text{Metarsenite ion}}{AsO_2^-} + 3Zn + 7H^+ \rightarrow 3Zn^{++} + \underset{\text{Arsine}}{AsH_3} \uparrow + 2H_2O$$

The arsine is carried away, as fast as formed, in a current of hydrogen

gas, produced by the action of the acid on the zinc. If the outlet tube from the hydrogen generator is heated at a constriction near its outer end the arsine is there decomposed, and elementary arsenic is deposited just beyond that point as a brilliant dark-brown or black mirror. As little as 0.1 mg of arsenic may readily be detected by this test. Antimony gives a similar mirror, distinguishable by being non-volatile and insoluble in a hypochlorite or hypobromite solution. (Ex. 17.)

In carrying out the Marsh test it is of the greatest importance to make sure that any dark stain that may be obtained is not due to traces of arsenic in the reagents used. Moreover, air must be displaced from the generator before the sample to be tested is added through the thistle tube; otherwise heating the outlet tube may produce an explosion.

Antimony and Bismuth

394. Salts of Antimony and Bismuth

The two elements immediately below arsenic in the Periodic Table are antimony and bismuth. These occur in nature both free and as sulfides. Antimony has some non-metallic properties, for salts of metaantimonic and pyroantimonic acids are well known. Bismuth, on the other hand, is exclusively metallic. No true bismuthates are known.

Both antimony and bismuth, unlike phosphorus and arsenic, form salts (acetates, carbonates, sulfates, etc.) in which the element behaves as a metal. In all these salts the metal is trivalent. Both antimony and bismuth, moreover, form salts containing a radical, (SbO) or (BiO), which acts like a univalent metal. These are the *antimonyl* and *bismuthyl* salts. We also have soluble *complex salts*, such as $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, potassium antimonyl tartrate, or *tartar emetic*, which is composed of K^+ and a complex antimonyl-tartrate anion.

All the antimony and bismuth salts react with water (hydrolysis, § 398), forming white precipitates (hydroxy-salts), which are mixtures of variable composition. Thus solutions of antimony trichloride and bismuth nitrate, on being poured into water, give precipitates which for simplicity may be represented by the approximate formulas SbOCl and $BiONO_3$. The other product in each reaction is hydrochloric or nitric acid:

$$SbCl_3 + H_2O \rightleftharpoons \underset{\text{Antimony oxychloride}}{SbOCl\downarrow} + 2HCl$$

Since these reactions are reversible, the precipitates may be redissolved by adding an excess of acid.

On account of hydrolysis it is impossible to have a clear solution of a bismuth or antimony salt, except in the presence of active mineral acids or else of certain organic substances, such as tartaric acid, that combine with the bismuth or antimony to form complex ions. (Ex. 18.)

395. Uses of Antimony and Bismuth

Antimony is one of the few substances that resemble water in expanding when solidifying. Its alloys with lead have the same property, and are accordingly used for type metal (Pb, 82; Sb, 15; Sn, 3). The expansion forces the alloy into every minute detail of the mold, giving a much sharper casting than could be obtained with such an alloy as brass. Antimony is also used in small quantities to toughen and harden lead, for storage-battery grids, piping, gutters, etc.

Babbitt metal, or anti-friction alloy, contains tin, copper, and antimony (Sn, 75 per cent; Sb, 12 per cent; Cu, 13 per cent). Its value depends on the fact that the solidified alloy consists of hard crystals, which take up most of the pressure, imbedded in a supercooled liquid that is yielding enough to distribute the pressure and make automatic adjustment for wear.

Bismuth is obtained commercially, as a by-product, in purifying lead. It is contained in small percentages in a good many anti-friction alloys, but is chiefly used in fusible alloys for electric fuses, plugs for automatic fire-alarms and automatic sprinkler systems, and as stereotype metal. Most of these fusible alloys contain about 50 per cent bismuth, with smaller amounts of lead and tin, and sometimes cadmium (*e.g.*, Wood's metal: Bi, 4; Pb, 2; Sn, 1; Cd, 1; m.p., about 60°C).

Exercises

1. What products are probably obtained in burning a match consisting chiefly of sulfur and potassium chlorate, assuming that the sulfur is oxidized to its highest valence state and the chlorate reduced to the lowest valence state of chlorine?

2. What products would you expect to obtain by the decomposition of ammonium phosphate at high temperatures?

3. Would you expect arsenic to resemble phosphorus or nitrogen in the number of acids that it forms? Why?

4. Write an electronic formula (§ 247) for orthophosphoric acid, in such a manner as to give each oxygen atom and the phosphorus atom an octet of electrons.

5. Write conventional equations for the neutralization of two molecules of phosphoric acid, in three successive steps, by calcium hydroxide, $Ca(OH)_2$.

6. Write a conventional equation for the preparation of dipotassium acid phosphate from orthophosphoric acid.

7. Write an equation for the action of sulfuric acid on apatite, giving hydrogen fluoride, calcium sulfate, and monocalcium phosphate.

8. Determine whether there is a change of valence number in converting arsenic trioxide into a metarsenite. Is this an example of oxidation-reduction?

9. Give the formulas of ammonium metarsenite and zinc metarsenite. Show how the latter may be prepared by precipitation (§ 193).

10. Write a conventional equation for the preparation of sodium metarsenite from sodium carbonate.

11. Write an electronic equation (§ 264) for the conversion of an arsenite into an arsenate. What change in valence number here occurs?

12. Represent the change just mentioned by a valence state equation (§ 266). How many liters of normal oxidizing solution (§ 294) are needed to accomplish the change, for the gram atom of arsenic here represented?

13. Write equations for the conversion of arsenic pentoxide into arsenic pentachloride, and for the hydrolysis (§ 391) of the latter, forming hydrochloric acid and orthoarsenic acid.

14. Write a valence state equation to represent the reduction of an arsenate to arsine. How many liters of normal oxidizing solution (§ 294) are needed to reverse the change here represented (1 gram atom of arsenic)?

15. Write a conventional equation for the production of Paris green precipitate by the action of solutions of two sodium salts on a solution of copper sulfate. What is the corresponding ionic equation (§ 193)?

16. What percentage of arsenic trioxide is contained in lead arsenate?

17. A milligram of elementary arsenic will produce what volume of gaseous arsine, under standard conditions?

18. Write an equation for a reaction in which antimony oxychloride dissolves in a solution of potassium acid tartrate to form tartar emetic.

To the Instructor

This seems an appropriate place to devote some thought to objectives. Our purpose has been to give the student the ability to read chemistry, wherever he may encounter it in his future training or work. Previous chapters have already given a sufficient vocabulary and disclosure of points of view to serve that purpose very well. If the most vital topics in what precedes have really been made familiar the able student, from this point onward, should be able to break ground for himself. It would be a mistake to assign the next two chapters to students not well grounded in the simpler fundamentals. Instead, the work of the semester might well be concluded by a survey of industrial applications, using these as illustrations of familiar general principles, wherever possible. The student who continues his training in chemistry may subsequently revert to the omitted chapters, to find in them an introductory qualitative glimpse of some ideas which chemical research is constantly seeking to make quantitative.

Chapter 29

HYDROLYSIS
HYDROGEN ION CONCENTRATION

396. Hydrolysis

In the practical applications of salts in industry one must constantly remember that many salts, merely by being dissolved in water, are partially or completely resolved into the acids and bases from which they are derived. For example, on dissolving aluminum chloride in water it is partially resolved into aluminum hydroxide (or a hydroxysalt, § 399) and hydrochloric acid:

$$\underset{\text{Salt}}{AlCl_3} + \underset{\text{Water}}{3HOH} \underset{\textit{Neutralization}}{\overset{\textit{Hydrolysis}}{\rightleftarrows}} \underset{\substack{\text{(Slightly}\\\text{active base)}}}{Al(OH)_3} + \underset{\substack{\text{(Active}\\\text{acid)}}}{3HCl}$$

The partial or complete conversion of a salt into an acid or base, by reaction with water, is an example of *hydrolysis*. Notice that *the hydrolysis of a salt is the reverse of neutralization.*

Hydrolysis, as applied to substances other than salts, means a reaction with water in which a given substance is transformed into other, *simpler* substances.

Equations of the type just given serve to identify the acid and base produced by the hydrolysis of any given salt. Yet the hydrolysis of an ionic salt frequently involves only one of its ions. So let us see how hydrolysis appears if we take note of ions. When an ionic salt dissolves in water its ions separately combine with the water to form *hydrated ions.*[1] The hydrated ions then lose or gain one or more protons:

1. Hydrated *cations of the heavy metals* (including hydrated Al^{+++}), also NH_4^+ and hydrated Mg^{++}) act as acids, transferring protons to

[1] A cation usually combines with 4 or 6 molecules of water, an anion with an indefinite or unknown number of molecules of water. For simplicity, in the next equation, only two molecules of water are indicated.

surrounding water molecules (or to any of the anions toward the end of the list on the next page):

$$Mg(H_2O)_2^{++} \rightleftharpoons Mg(OH)_2 + \underset{\text{Transferred}}{2H^+}$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + \underset{\text{Transferred}}{H^+}$$

So we obtain a *slightly active base* and an acid. The identity of the acid is determined by the anion furnished by the salt. The hydrolysis of magnesium sulfate, for example, yields sulfuric acid, that is, the ions H_3O^+ (from transfer of H^+ to H_2O) and SO_4^{--} (derived, unchanged, from the salt).

2. Hydrated *anions of all but the most active acids* act as bases, gaining protons from water (or from the hydrated cations which we have just recognized as acids):

$$\overbrace{CO_3^{--} \quad + \quad H_2O}^{H^+\ \text{(transferred)}} \rightleftharpoons HCO_3^- + OH^-$$

$$\overbrace{HCO_3^- \quad + \quad H_2O}^{H^+\ \text{(transferred)}} \rightleftharpoons H_2CO_3 + OH^-$$

The result is a *slightly active acid* and a base (whose identity is determined by the cation of the salt). The hydrolysis of sodium carbonate, for example, yields sodium hydroxide, namely the ions Na^+ (derived, unchanged, from the salt) and OH^- (produced in the manner just shown). (Ex. 1–3.)

397. Reaction of Salt Solutions Toward Indicators

Solutions of many salts whose formulas do not suggest acid or alkaline properties nevertheless react acid or alkaline toward indicators because of hydrolysis. By observing what ions are present we may determine what the reaction of any given salt should be:

1. Hydrated cations of the heavy metals, also hydrated Al^{+++}, Mg^{++}, and NH_4^+, are *acids* and react acid toward most indicators.

2. Hydrated anions of all but the most active acids are *bases*. To infer their reaction toward different indicators, let us arrange them *in the order of increasing activity as bases* [2]:

[2] The anions in this list that happen to contain hydrogen (HSO_4^-, for example) also act as acids, when in the presence of sufficiently active bases.

HSO_4^-	HSO_3^-	$H_2PO_4^-$	F^-
Hydrogen sulfate ion (Acid toward all common indicators)		Dihydrogen phosphate ion	

(Alkaline toward methyl orange, decreasingly acid toward phenolphthalein)

$C_2H_3O_2^-$	SO_3^{--}	HCO_3^-	HS^-	HPO_4^{--}	CN^-	BO_2^-	CO_3^{--}	PO_4^{---}	OH^-	S^{--}
		Hydrogen carbonate ion		Mono-hydrogen phosphate ion				Phosphate ion		

Strongly alkaline toward methyl orange; increasingly alkaline toward phenolphthalein)

3. Most other hydrated ions (cations of the alkali and alkaline-earth metals, except Mg^{++}; anions of active acids) are neither acids nor bases, hence are *inert*, in other words, do not affect indicators.

When one of the ions of a salt is inert, the reaction of solutions of the salt toward indicators is determined by the other ion, and can be told at a glance. Examples:

Acid (*Anion inert*)	*Alkaline* (*Cation inert*)	*Neutral* (*Both ions inert*)
$CuSO_4$	Na_2CO_3	$NaCl$
$Fe(NO_3)_3$	CaS	K_2SO_4
$ZnCl_2$	$KHCO_3$	$Ca(NO_3)_2$
$MgCl_2$	K_2HPO_4	$Ba(ClO_4)_2$

If one of the hydrated ions of a salt reacts acid and the other alkaline, we need to know which of these is the more active, or need to make an actual test in the laboratory to determine how a solution of the salt will react toward indicators. Examples: $Mg(C_2H_3O_2)_2$, NH_4F. (Ex. 4–7.)

398. How to Decrease or Increase Hydrolysis

In the practical applications of salts we sometimes need to decrease hydrolysis and sometimes to increase it. For example, solutions of readily hydrolyzable salts of the heavy metals sometimes become cloudy on standing, from the separation of a precipitate of the heavy-metal hydroxide or a hydroxy- or oxy-salt (§ 399), formed by hydrolysis:

$$FeCl_3 + 3H_2O \underset{(b)}{\overset{(a)}{\rightleftharpoons}} Fe(OH)_3 \downarrow + 3HCl$$

$$SbCl_3 + H_2O \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \underset{\substack{\text{Antimony}\\\text{oxychlo-}\\\text{ride}\\\text{(an oxy-salt)}}}{SbOCl \downarrow} + 2HCl$$

When an excess of an acid (hydrochloric acid, in the two examples here given) is added to the mixture, the reverse reaction (*b*) is favored (mass action, § 338) and the precipitate is redissolved; or if acid is added in the beginning, precipitation may be prevented.

It is common practice to add an excess of acid to solutions of heavy-metal salts, whenever experience shows that hydrolysis is likely to produce a precipitate. Salts of tin, antimony, and bismuth need a considerable excess of acid to prevent precipitation; salts of mercury, ferric iron, chromium, and aluminum need a somewhat smaller excess. If both the ions of a salt are subject to hydrolysis the hydrolysis is practically complete unless prevented by the addition of a considerable excess of acid.

On the contrary, hydrolysis is desired in certain industries, for example, in using heavy-metal salts as *mordants*, to fix dyestuffs in fabrics. The fixation of the dye is brought about by hydroxy-salts, produced by hydrolysis and deposited in the fibers. Hydrolysis is also favored by *boiling* the solution, whenever the acid set free is somewhat volatile:

$$\underset{\substack{\text{Ferric}\\ \text{acetate}}}{Fe(C_2H_3O_2)_3} + H_2O \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \underset{\substack{\text{Ferric hydroxy-}\\ \text{acetate}\\ \text{(a hydroxy-salt)}\\ \text{(precipitated)}}}{Fe(OH)(C_2H_3O_2)_2 \downarrow} + \underset{\substack{\text{Escapes}\\ \text{with}\\ \text{steam}}}{HC_2H_3O_2 \uparrow}$$

Since acetic acid is volatile and escapes with the steam when the solution is boiled, the reverse reaction (*b*) is to that extent prevented. In the end the dissolved ferric salt is completely precipitated as a hydroxy-salt. This, by prolonged boiling or in the presence of alkalies, may gradually be converted into ferric hydroxide, $Fe(OH)_3$. (Ex. 8–13.)

399. Hydroxy- or Oxy-Salts

We have just seen that hydrolysis sometimes results in a hydroxy- or oxy-salt. Salts of this nature are intermediate in composition between ordinary "normal" salts and hydrous oxides (sometimes termed "hydroxides of the heavy metals," § 192, item 2):

Normal Salts	*Hydroxy-Salts*	*Hydrous Oxides*
$ZnCl_2$	$Zn(OH)Cl$	$Zn(OH)_2$
$Fe(C_2H_3O_2)_3$	$Fe(OH)(C_2H_3O_2)_2$	
	$Fe(OH)_2(C_2H_3O_2)$	$Fe(OH)_3$

So, if we add an alkali (sodium or potassium hydroxide) to a solution of a heavy-metal salt, we ordinarily first precipitate a *hydroxy-salt*, which is gradually converted into a *hydrous oxide*, as more alkali is added. Similarly, when a dissolved heavy-metal salt of a volatile acid is hydrolyzed by persistent boiling (the volatile acid escaping with the steam, § 398), a hydroxy-salt is first formed, which is then gradually converted into a hydrous oxide.

Yet the formulas just given do not disclose what really happens in such reactions. Dissolved heavy-metal cations are *hydrated* and function as *acids* (§ 396). As these hydrated cations yield protons to an added alkali (or form molecules of an escaping volatile acid), their charge is gradually reduced. Observe, for example, how the charge on hydrated ferric ion (present in a solution of any ferric salt) is gradually reduced toward zero, as it yields protons:

Cation of Normal Salt		*Cation of Hydroxy-salt*				*Hydrous Oxide*
$n\mathrm{Fe(H_2O)_6}^{+++}$	$\rightarrow$	$[\mathrm{Fe(H_2O)_5(OH)}]_n{}^{++}$	$\rightarrow$	$[\mathrm{Fe(H_2O)_4(OH)_2}]_n{}^{+}$	$\rightarrow$	$[\mathrm{Fe(H_2O)_3(OH)_3}]_n$
	$\searrow n\mathrm{H}^+$ (transferred)		$\searrow n\mathrm{H}^+$ (transferred)		$\searrow n\mathrm{H}^+$ (transferred)	

The brackets, $[\quad]_n$, in these formulas are intended to indicate that an indefinite number, n, of simple cations of reduced charge may become linked through intervening molecules of water to form positively charged networks or "giant cations." Many intermediate steps are therefore possible in forming a hydroxy-salt, between the steps just shown, as the giant cations gradually have their charge reduced by yielding protons. The anions that are present along with the giant cations in all hydroxy-salts are of course ordinary simple anions (Cl^-, $\mathrm{C_2H_3O_2}^-$, etc.), depending on which heavy-metal salt was originally present.

Hydroxy-salts prepared by either of the methods just described are of course usually *complex mixtures* of different compounds that correspond to the indefinite number of successive steps in the hydrolysis. By loss of water, most of them may be converted into oxy-salts, just as hydrous oxides, by loss of water, are converted into ordinary anhydrous oxides.

Though hydroxy- and oxy-salts are usually of variable composition, there are some (including many minerals) which contain a definite amount of combined water of hydration, or a definite proportion of hydroxyl or oxide ions, occupying definite positions in the crystal structure.

400. Titration of a Base by an Acid

A *titration* is an experiment in which we determine what volume of a solution is needed to react with a specified volume or weight of something else. An important example is the titration of an acid by an alkali. The acid and alkali are ordinarily contained in slender tubes called burets (Fig. 130), each usually having a total capacity of 50 or 100 ml, and being graduated in milliliters and tenths of a milliliter.

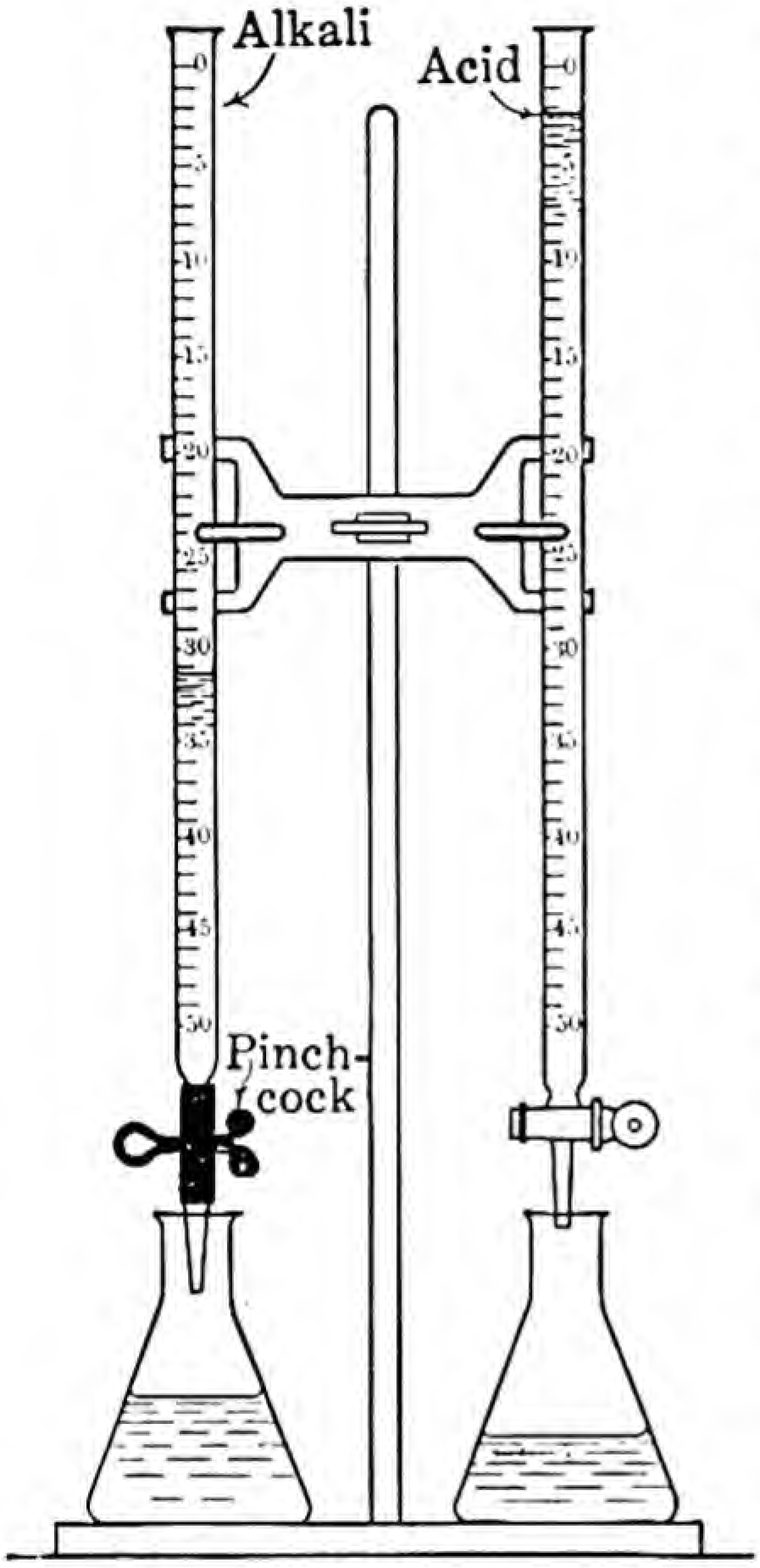


FIG. 130. Burets. Observe that the solution of alkali is contained in a buret that is closed with a rubber tube and pinchcock, since a glass stopcock often sticks fast when wet with an alkali.

One of the two solutions may be of known concentration. A definite volume of this solution is drawn from the buret into a beaker. Then we add a few drops of a solution of an indicator. We now add the other solution from the other buret, rapidly at first, then slowly and drop by drop, stirring the liquid constantly, until we reach the *titration end point* (the point at which the indicator solution shows the least perceptible change in color). From the relative volumes of the two solutions we can calculate the concentration of either solution if that of the other is known.

It is important to titrate from the less intense or less readily perceived to the more intense or more readily perceived color of the indicator. Thus the red color that the indicators methyl orange and methyl red possess in an acid solution is more readily perceived than the yellow color they possess in an alkaline solution. One therefore starts with a measured quantity of alkaline solution in the beaker and draws acid into this from the buret, until the indicator changes from yellow to the least perceptible shade of pink. To proceed in the reverse manner, adding an alkaline solution to an acid solution until the pink color fades to yellow, is to risk overstepping the end point by several tenths of a milliliter.

The acid molecules and hydrogen ions in a solution of a slightly active acid are interconvertible:

$$\underset{\text{Acid molecules}}{HC_2H_3O_2} + H_2O \rightleftharpoons \underset{\text{Hydrogen ions}}{H_3O^+} + C_2H_3O_2^-$$

So it makes no difference whether an alkali added in titration is considered as reacting with acid molecules or with hydrogen ions, or with both. Since these are interconvertible, *they are both neutralized.* In brief, *titration measures the total acidity of a solution*, regardless of whether the dissolved acid is active (hence chiefly present as hydrogen ions) or very slightly active (hence chiefly present as acid molecules). (Ex. 14, 15.)

401. Total Acidity vs. Hydrogen Ion Concentration

In industrial applications in which acids neutralize bases we are interested in the *total acidity*, as determined by titration. But there are other applications in which the *activity* (or *strength*) of the acid is important. When an acid is to be used as a catalyst, in the hydrolysis of cane sugar (which converts it into two other sugars, glucose and fructose), or in the conversion of starch into glucose, an active acid such as hydrochloric acid is much more effective than a slightly active one such as acetic acid.

We have seen (§ 187) that the more active and the more dilute an acid is, the more of it is present as ions in a solution in water:

$$\underset{\text{Acid molecules}}{HC_2H_3O_2} \xrightarrow{H^+ \text{ (transferred)}} H_2O \rightleftharpoons \underset{\text{Hydrogen ions}}{H_3O^+} + C_2H_3O_2^-$$

So the concentration of hydrogen ion, H_3O^+, in a solution of an acid depends on the *total concentration* of the acid and also on its *activity* (which is somewhat dependent on the temperature).

The hydrogen ion concentration of a dilute acid solution is roughly indicated by its *sourness*. If cranberry juice appears sourer than strawberry juice you will know that the former contains a higher *hydrogen ion concentration*. It would therefore invert a sugar solution the more rapidly. But titration of the two juices with an alkali might reveal strawberry juice to have a higher *total acidity* (including both acid molecules and hydrogen ions).

There are three chief methods for determining hydrogen ion concentration:

1. The hydrogen ion concentration of a dilute acid solution may (in the absence of salts) be inferred from its electrical conductivity. An example will be given in § 410.

2. A second method for determining the hydrogen ion concentration of a solution is to observe the color that it develops with a properly chosen indicator (details in § 406).

3. The third and most accurate method for determining hydrogen ion concentration makes use of the *hydrogen electrode,* about to be described.

402. The Hydrogen Electrode

The hydrogen ion concentration of a solution may be most accurately measured with the aid of an instrument called the *hydrogen electrode,* dipping into the solution. The electrode itself consists of a small strip of platinum or gold (Fig. 131), covered with a thin deposit of finely divided platinum (platinum black), and in contact with *purified hydrogen gas,* as well as with the solution to be tested.

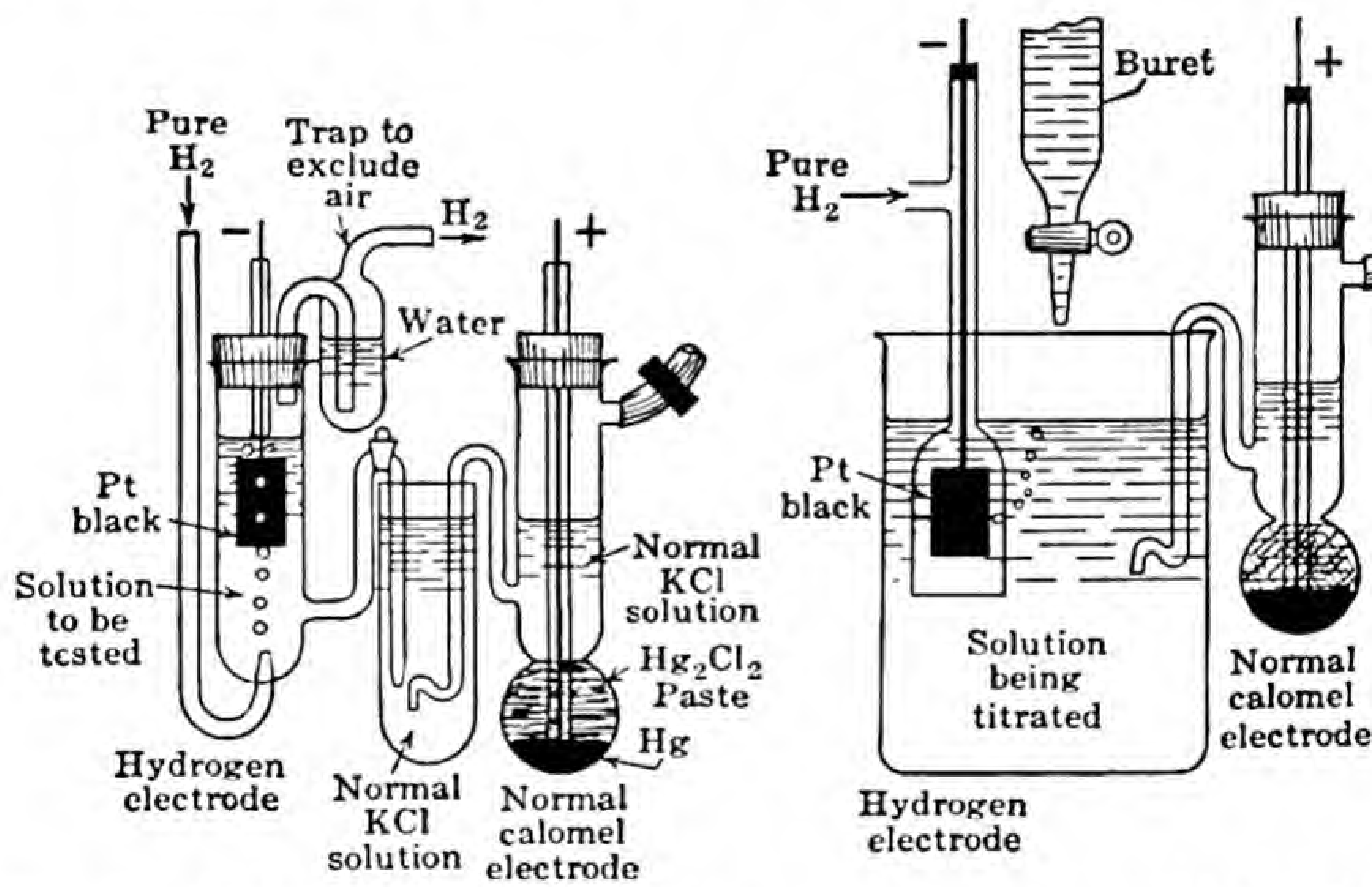


FIG. 131. The hydrogen electrode. The arrangement shown at the left is suited to the determination of the pH of a solution that is not to be neutralized. The one at the right permits the pH of a solution to be determined at the end of each of a number of successive additions of alkali, thus obtaining data for plotting a "titration curve," shown in Figs. 132, 133, p. 460.

The platinum black catalyzes the transformation of the hydrogen gas into monatomic hydrogen, H. This in turn is in equilibrium with the hydrogen ions of the solution.

$$\underset{\substack{\text{Catalyzed by}\\ \text{platinum black}}}{H_2 \rightleftharpoons 2H} \quad \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \quad 2H^+ + \underset{\substack{\text{Transferred}\\ \text{to solvent,}\\ \text{forming } H_3O^+}}{2e}$$

Any *decrease* in the concentration of the hydrogen ions in the solution will favor reaction (*a*), releasing electrons, which will accumulate in the electrode and make the electrode more negative. Any *increase* in the concentration of hydrogen ions will favor reaction (*b*), which by withdrawing electrons from the electrode will make the electrode more positive. So if in any manner we contrive to measure the *potential* (p. 614) of the electrode, in volts, we may infer the hydrogen ion concentration, $[H_3O^+]$, of the solution into which the electrode dips. The *normal calomel electrode*, shown in Fig. 131, consists of metallic mercury, covered with a paste of calomel, Hg_2Cl_2, in equilibrium with a normal solution of potassium chloride.

403. The Ionization of Water

The unstable complexes or "giant molecules" constituting liquid water (§ 250) are in constant agitation, their energy of motion being determined by the temperature. When two of them collide, a proton may be transferred from one to the other. Any molecule thus acquiring a proton becomes positively charged, and any one losing a proton becomes negatively charged. The simplest case would be

$$\overset{H^+}{H_2O + H_2O} \rightleftharpoons H_3O^+ + OH^-$$

in which oxonium ion and hydroxyl ion are produced; but more complex ions are possible.

The existence of ions in water is indicated by the fact that even the most carefully purified water has a definite, slight conductivity. Measurements of the conductivity of highly purified water and a study of equilibria in which water plays a part (hydrolysis) indicate an ion-concentration at room temperature (25°C) corresponding to the formation of *one pair of ions*, in the reaction formulated above, for about every 550,000,000 molecules of water. This is 1 gram ion (19 grams) of H_3O^+ and 1 gram ion (17 grams) of OH^- for every 550,000,000 moles of water, or for every 10,000,000 liters of water. Otherwise expressed, *the hydrogen ion activity of water, at 25°C, is one ten-millionth* (10^{-7}) *gram ion per liter. This corresponds to a ten-millionth normal solution of an active acid, completely ionized.*

As the temperature increases, the molecules and molecular groups of water vibrate more and more violently, and collisions between them more frequently result in the transfer of protons, forming ions. At 0°C the hydrogen ion activity of water is about 0.34 times the value just indicated for 25°C, and at 50°C it is about 2.35 times that value. (Ex. 16.)

404. The Ion-Product for Water

In the ionization of water a hydroxyl ion is formed for every oxonium ion. A neutral solution may therefore be defined as one in which the hydrogen ion concentration and hydroxyl ion concentration are equal (each having the value 10^{-7} gram ion per liter, at 25°C). An *acid solution* (in water as a solvent) is one in which the hydrogen ion concentration rises above and the hydroxyl ion concentration falls below 10^{-7} gram ion per liter. An *alkaline solution* (in water as a solvent) is one in which the hydrogen ion concentration falls below and the hydroxyl ion concentration rises above 10^{-7} gram ion per liter.

In the equilibrium

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

the two opposing reaction rates must be equal, in order to have equilibrium at any given temperature. The rate of the forward reaction is determined by the temperature. But that of the reverse reaction is proportional to the product of the two concentrations $[H_3O^+] \times [OH^-]$. So, if $[H_3O^+]$ is in any manner *increased*, evidently $[OH^-]$ must *decrease* in the same proportion, if the reverse reaction is to continue just to balance the forward reaction.

Otherwise expressed, the *product of the two ion concentrations* $[H_3O^+] \times [OH^-]$, *in any aqueous solution, has a definite value at each temperature* ($10^{-7} \times 10^{-7} = 10^{-14}$, at 25°C) *whether the solution is acid, neutral, or alkaline.* The product of the concentrations $[H_3O^+] \times [OH^-]$ is often called the *ion-product for water* (at some specified temperature). Activities are expressed in gram ions per liter. (Ex. 17.)

405. The *p*H Scale

The hydrogen ion concentration of solutions that are only faintly acid or even alkaline is conveniently expressed by the **hydrogen ion index** or ***p*H.**[3] This is the exponent of 10, with sign reversed, in the

[3] The symbol *p*H (pronounced *pee-aitch*) implies that the hydrogen ion index is measured by the *potential* (*p.* 614) *of a hydrogen electrode*, in equilibrium with the given solution.

hydrogen ion activity.[4] Thus when the hydrogen ion activity is 10^{-9} the pH is 9. As the hydrogen ion activity (or concentration) of a solution *increases* its pH *decreases*, and conversely.

Hydrogen Ion Activity		pH
10^{-11}	↑ Increasing alkalinity	11
10^{-10}		10
10^{-9}		9
10^{-8}		8
10^{-7}	neutral	7
10^{-6}	Increasing acidity ↓	6
10^{-5}		5
10^{-4}		4
10^{-3}		3

A neutral solution has a pH of 7. A pH less than 7 indicates an acid solution; one more than 7 indicates an alkaline solution, as shown in the small table in the margin of this page.

Values of pH intermediate between whole numbers are found by observing that *the pH may be defined as the logarithm (with sign reversed) of the hydrogen ion activity.* Consider, for example, a solution with a hydrogen ion activity of 4×10^{-9}. The hydrogen ion activity is here *greater* than that of a solution of $p\text{H} = 9$; the pH must therefore be *less* than 9 by $\log 4 = 0.6$. Hence the pH is $9 - 0.6 = 8.4$. (Ex. 18, 19.)

406. Indicators

An *indicator* is a substance which in some manner makes evident the presence of another substance or the completion of a chemical reaction. We are here concerned with *acid-base indicators*—those that display a change in color whenever the hydrogen ion activity of the surrounding medium is sufficiently altered. Indicators of this class are always themselves either slightly active acids or slightly active bases.

The different colors shown by an indicator correspond to different arrangements of atoms within its molecule. One arrangement results in a molecule with the properties of an acid or base. The other form is practically non-ionized. If we represent the non-ionizable form of an indicator-acid (such as phenolphthalein) by (HX) and the ionizable form by H·X, the equilibrium existing in a solution of an indicator-acid in water may be formulated:

$$\underset{\substack{\text{Non-ionizable}\\ \text{form (obtained}\\ \text{in acid solution)}}}{(HX)} \underset{(d)}{\overset{(c)}{\rightleftharpoons}} \underset{\substack{\text{Ionizable}\\ \text{form}}}{H\cdot X}$$

$$+$$

$$H_2O \underset{(b)}{\overset{(a)}{\rightleftharpoons}} H_3O^+ + \underset{\substack{\text{Ion of indicator salt}\\ \text{(obtained in alkaline}\\ \text{solution)}}}{X^-}$$

[4] Activity here means "effective concentration," explained hereafter (§ 419).

Adding an alkali to a solution containing the indicator will remove H_3O^+, and thus render reaction (*a*) more nearly complete (Principle of Mass Action, § 338). The consequent decrease in the concentration of H·X will render reaction (*c*) more nearly complete. So, in the end, most of the non-ionizable form (HX) may disappear, and the solution will show the color characteristic of the ion, X^-, of the indicator salt.

Characteristics of the Most Important Indicators

For most of these indicators, 1 or 2 drops of a 1 per cent indicator solution should be used for every 10 ml of solution to be titrated.

The mid-point of the *p*H range of an indicator is the *p*H at which its acid and alkaline forms are present in equal concentrations. It is numerically equal to the pK_a (§ 409) of the indicator acid.

	Acid Color	*pH Range*	*Alkaline Color*	*pH at End Point (Defined, p. 452)*
Thymol blue (acid range)	Red	1.2– 2.8	Yellow	2.6
Tropeolin 00	Red	1.3– 3.2	Yellow	2.8
Methyl yellow	Red	2.9– 4.0	Yellow	4.0
Bromophenol blue	Yellow	3.0– 4.6	Blue	4.0
Methyl orange	Red	3.1– 4.4	Orange-yellow	4.0
Sodium alizarin sulfonate	Yellow	3.7– 5.2	Violet	4.3
Bromocresol blue	Yellow	4.0– 5.6	Blue	4.8
Methyl red	Red	4.4– 6.3	Yellow	5.0
Chlorophenol red	Yellow	5.0– 6.6	Red	5.7
Bromocresol purple	Yellow	5.2– 6.8	Purple	6.0
Bromothymol blue	Yellow	6.0– 7.6	Blue	6.8
Rosolic acid	Brown	6.9– 8.0	Red	7.4
Phenol red	Yellow	6.8– 8.0	Red	7.5
Neutral red	Red	6.8– 8.0	Yellow	7.0
Cresol red	Yellow-purple	7.2– 8.8	Red	8.0
Thymol blue (alk. range)	Yellow	8.0– 9.6	Blue	8.8
Phenolphthalein	Colorless	8.2–10.0	Red	9.0
Thymolphthalein	Yellow	9.3–10.5	Blue	10.0
Nitramin	Colorless	11.0–13.4	Orange-brown	11.6
Mixed indicators:				
1 gram methyl orange and 2.5 grams indigo carmine in 1 liter water.	Violet	3.1– 4.4	Yellow-green	4.0
1 gram bromocresol purple, 1 gram bromothymol blue, in 200 ml warm alcohol; dilute with water to 500 ml.	Yellow	6.0– 8.0	Blue	6.7

For demonstration experiments with universal indicators see *J. Chem. Educ.* **14,** 274.

The addition of an acid to the solution favors the reverse reactions (*b*) and (*d*), and finally may cause both X^- and $H \cdot X$ largely to disappear. The solution then shows the color characteristic of the non-ionizable form (HX). With phenolphthalein, the indicator ion, X^-, is red, and the non-ionizable form (HX) is colorless.

The actual hydrogen ion activity needed to cause a change in color will, of course, depend (1) on whether a solution of the indicator in pure water is predominantly (HX) or $H \cdot X$; (2) on the ionization constant of $H \cdot X$, considered as an acid; (3) on the relative intensities of the two colors. *Each indicator changes color within a particular range of hydrogen ion activity or pH, and commonly not in a precisely neutral solution.*

Phenolphthalein, for example, just begins to develop a pink color at a *p*H of about 8.2; and as the solution becomes more and more alkaline the pink color grows more and more intense, becoming fully developed at a *p*H of about 10.0, as shown in the table on p. 458.

The hydrogen ion activity (or the pH) of a solution may therefore be determined (usually within one or two tenths of a unit) by adding one or two drops of an appropriately chosen indicator, then noting the color, in comparison with that shown by the same indicator in solutions of known pH, within the range to which the indicator responds. (Ex. 20.)

407. Titration Curves

Let us measure out a 30-ml sample of a 0.2*N* acid and titrate it with a 0.2*N* alkali, slowly added from a buret. After each addition of alkali we stir the solution, then determine its *p*H, with the aid of the hydrogen electrode.

The result is shown in Fig. 132. The left-hand portion of the curve, representing the early part of the titration, with acid still in excess, has a shape that depends on the nature of the acid used. It will be as given by the curve *A* with a strong (active) acid, and as given by *A′* or *A″* with a weak (slightly active) acid. After the neutral point (represented by the vertical line *N*) has been passed an excess of base accumulates in the solution. The shape of the curve then depends on the nature of base. It will be as given by *B* with a strong (active) base, and as given by *B′* or *B″* with a weak (slightly active) base.

We see that the addition of alkali to the acid does not alter the *p*H of the solution very much until a large portion of the acid has been neutralized. Further addition of alkali then causes the *p*H to rise more and more rapidly, until at the neutral point, *N*, a single drop of alkali may cause the *p*H to increase by as much as five or six units (when titrating a strong acid with a strong base, along the curve *AB*).

A number of horizontal bands have been drawn across the diagram, showing the range of *p*H within which various indicators change color.

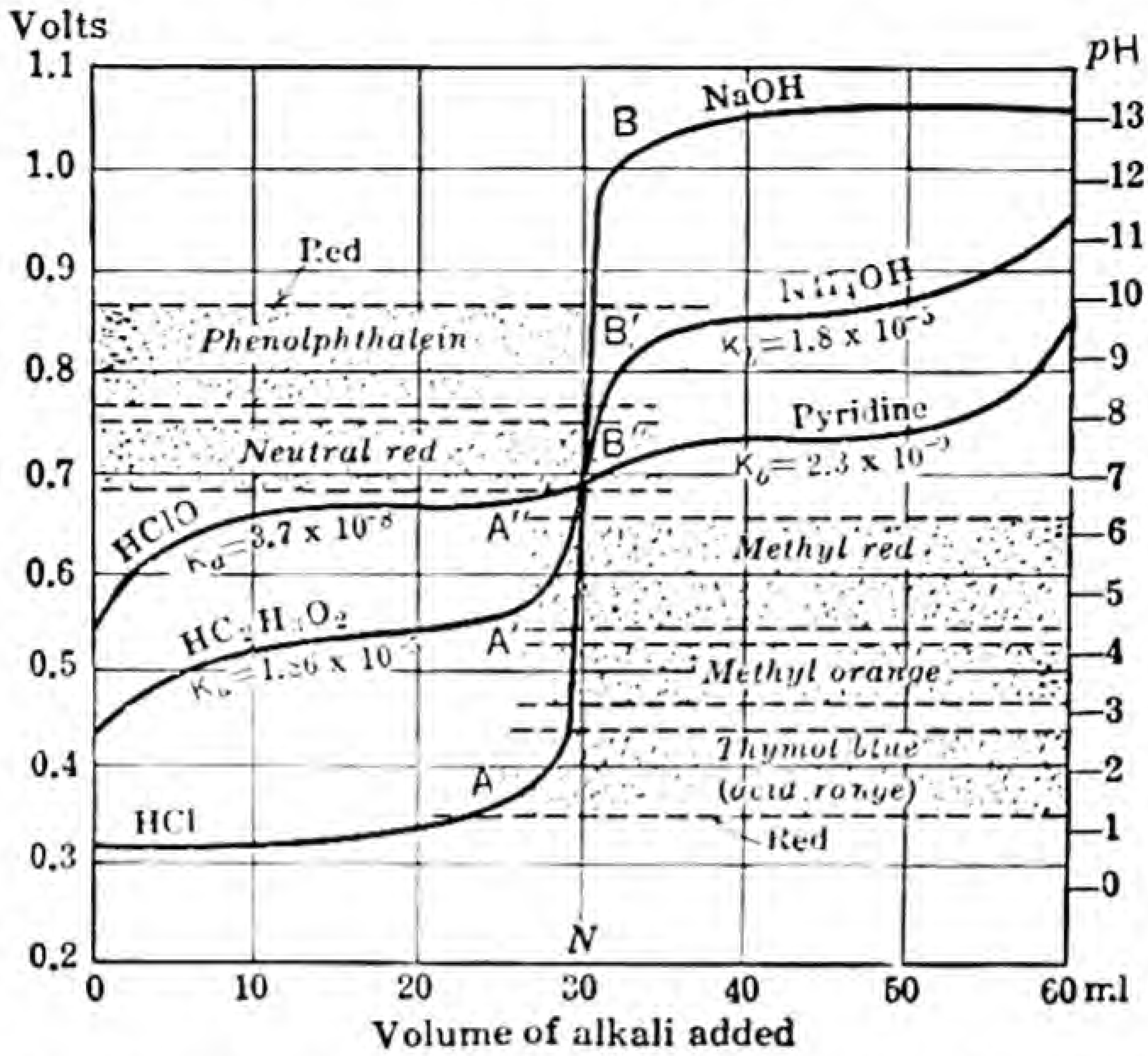


FIG. 132. Titration curves in the presence of various indicators.

At the lower edge of each band the indicator has its acid color (colorless, for phenolphthalein). At the upper edge of each band the indicator has its alkaline color (pink, for phenolphthalein).

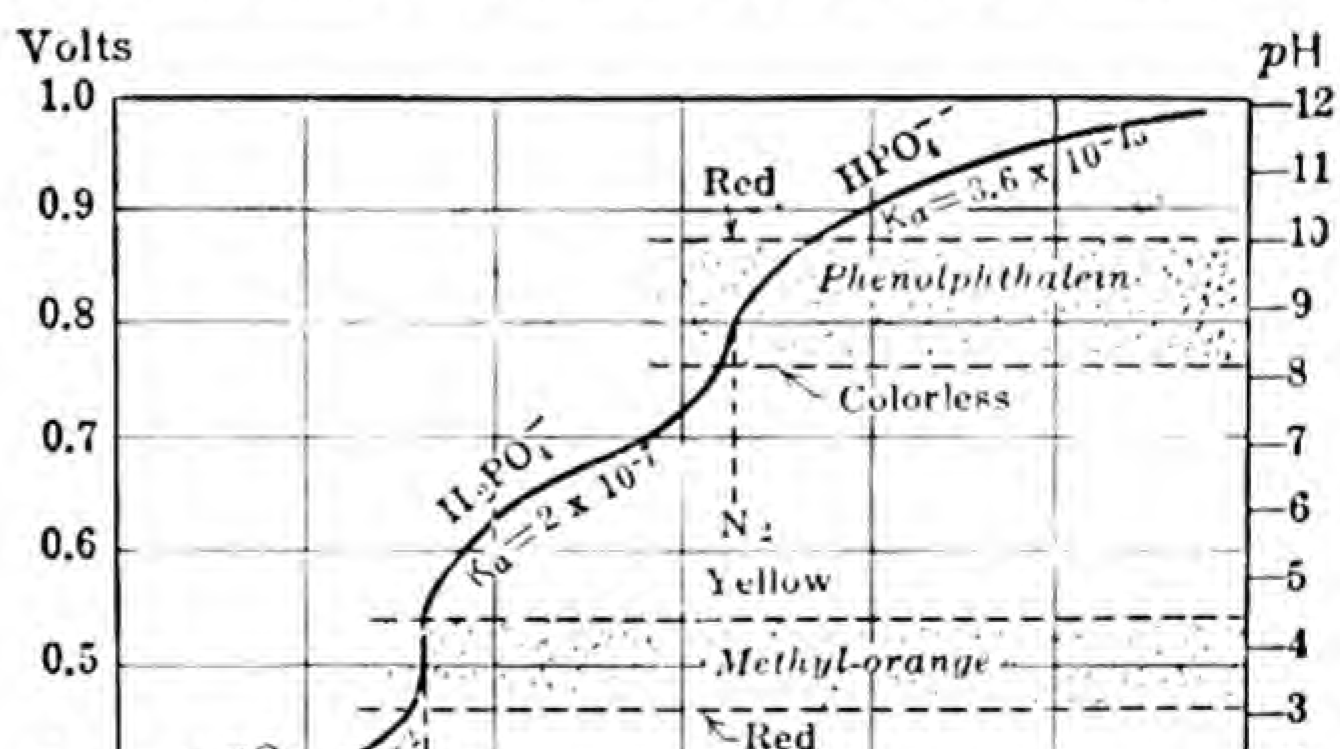


FIG. 133. A titration curve, showing the way in which the *p*H varies, as a standard solution of phosphoric acid is titrated with an alkali.

In Fig. 133 we see the result of titrating a triprotic acid, H_3PO_4, with an alkali. Observe two distinct rises in *p*H, corresponding to the addition of enough alkali to remove the first and second protons in

H_3PO_4. The end of the third stage of the neutralization is not detectable when water is the solvent. Observe that the different stages in this titration call for different indicators. (Ex. 21.)

408. Choice of an Indicator in Titration

The preceding titration curves indicate some principles that should determine the choice of an indicator in titration:

1. If we are titrating a *strong acid* with a *strong base* (curve AB in Fig. 132) the titration curve rises so sharply at the end point (neutral point) that it cuts almost vertically across most of the indicator bands. This means that *almost any indicator can be used in the titration of a strong acid by a strong base.*

2. In titrating a *weak acid* with a *strong base* (curve $A'B$ or $A''B$ in Fig. 132) the sudden rise in pH at the end point is very much less pronounced. It still cuts nearly vertically through the bands for *phenolp thalein* and one or two other indicators, hence these indicators will serve.

But the titration curves just mentioned intercept the bands for methyl orange or methyl red on an angle. In consequence, methyl orange or methyl red change color only gradually, during addition of several cubic centimeters of alkali, instead of sharply, with a single drop of alkali. Worse yet, the bands for these two indicators are intercepted by $A'B$ and $A''B$ before the neutral point is reached; so the color change with these indicators not only is *too gradual* but also occurs *too early.*

3. The titration of a *strong acid* by a *weak base* (curve AB' or AB'') obviously calls for an indicator which changes color in a somewhat acid solution; in other words at a pH of somewhat less than 7, the actual choice depending on the ionization constant of the base. *Methyl orange* or *methyl red* will ordinarily serve.

4. The titration of a *weak acid* with a *weak base* (some combination of curve A' or A'' with B' or B'') results in such a slight increase of pH at the end point that the indicator needs to be chosen with care, by calculation (details in § 415). Sometimes no indicator will serve very well. We may then be compelled to plot the entire titration curve with the aid of a hydrogen electrode. The end point is the point at which we get the most rapid increase in pH. (Ex. 22.)

409. The Ionization Constant

The equilibrium constant (§ 340) of any reaction in which ions are formed is usually called an *ionization constant.* Consider the

ionization of any slightly active acid, which we shall represent by the general formula HX:

$$\underset{\substack{\text{Acid}\\ \text{molecules}}}{HX} + H_2O \rightleftharpoons \underbrace{H_3O^+ + X^-}_{\text{Acid ions}}$$

Using brackets to stand for the words "concentration of" the ionization constant of this acid is

$$K_a = \frac{[H_3O^+] \times [X^-]}{[H_2O] \times [HX]}$$

Concentrations are expressed in *moles per liter* for the acid molecules and in *gram ions per liter* for the acid ions. The concentration of the water in dilute solutions is practically the same as in pure water, hence is represented by 1 (§ 340), and need not be included in the expression for the ionization constant. (Ex. 23, 24.)

If the ions H_3O^+ and X^- in the solution are both furnished exclusively by the ionization of the acid HX, they are of course produced in equal numbers, hence $[H_3O^+]$ and $[X^-]$ in our equation must be equal. But frequently *some other acid* may furnish part of the H_3O^+, and a *salt* of the given acid may furnish part of the X^-. The $[H_3O^+]$ and $[X^-]$ in our equation will then no longer be equal. We always employ the *total concentration* of any ion in the equation, regardless of its source.

As a solution of a slightly active acid in water is more and more diluted, the acid is more and more converted into ions; but the consequent changes in the concentration of the acid molecules, HX, and in the ions H_3O^+ and X^-, are in such proportions that *the ionization constant remains unchanged, as long as the temperature is unchanged.* We may even add some other acid (hence an excess of H_3O^+) or a salt of the given acid (hence an excess of X^-) without altering the ionization constant of the acid. In brief, *the ionization constant of a slightly active acid depends only on the identity of the acid and on the temperature.* It does not depend on the concentration of the acid (provided that the concentration is not very great).

The ionization constant of an acid is a measure of its *strength* or reactivity. A very small value of the ionization constant (7.2×10^{-10}, for example) indicates that the acid is only slightly active, hence reacts only incompletely with water, and so exists very largely as neutral molecules rather than as ions, even when very greatly diluted with water.

Ionization constants for a number of important acids and bases are given in Appendix I. Referring to this, we see that sulfurous acid and phosphoric acids, for example, have ionization constants of the same general order. So sulfurous acid, in applications which chiefly depend on acid strength, might conceivably be replaced by phosphoric acid. The table in the appendix includes only *moderately active* and *slightly active* acids, since active acids, on being dissolved in water, are practically completely converted into ions. In brief, the ionization constant of an *active* acid is indefinitely large.

The ionization constant of a hydroxide, such as ammonium hydroxide, serving as a base, would be written:

$$K_b = \frac{[NH_4^+] \times [OH^-]}{[NH_4OH]}$$

Recently *the logarithm (with sign reversed) of the ionization constant* has been used as a measure of strength or reactivity. This is the *acid* or *base exponent*, represented by pK_a or pK_b, respectively. A value near 0 indicates a strong or active acid or base; a value much higher than 0 indicates an acid or base that is correspondingly weak. For a substance that is as weak an acid as water, pK_a is 14. For one that is as weak a base as water, pK_b is 14.

It is worth observing that $14 - pK_b$ is the pK_a, in solution in water, of the acid derived from the given base by direct union with a proton (as discussed in § 413).

410. Calculations Based on the Ionization Constant

Most of the ionization constants in Appendix I were determined by measurements of the conductivity of dilute solutions of the acids. For example, in the ionization of acetic acid each mole of acid ionized produces a gram ion of each of the two ions, H_3O^+ and $C_2H_3O_2^-$. So a $N/10$ solution of acetic acid, *fully ionized*, would contain 0.1 gram ion of each ion, in 1 liter of solution. The total conductivity of such a solution can easily be calculated, for it is the sum of the conductivities which would separately be given to it by 0.1 gram ion of H_3O^+ and 0.1 gram ion of $C_2H_3O_2^-$.

But the actual conductivity of a $N/10$ solution of acetic acid, at 25°C, is only 1.3 per cent of that calculated. We therefore conclude that the acid in a $N/10$ solution is only 1.3 per cent ionized, and that the concentration of each ion is $0.013 \times 0.1 = 0.0013$ gram ion per liter. The concentration of the acid molecules is the total concentra-

tion minus the portion ionized, namely 0.1 − 0.0013 = 0.0987 gram ion per liter.

Substituting these values in the expression for the ionization constant, we find that the constant for acetic acid, at 25°C, is

$$K_c = \frac{[H_3O^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{0.0013 \times 0.0013}{0.0987} =$$

$$1.8 \times 10^{-5}, \text{ approximately}$$

Of course we could turn this calculation around and use an ionization constant, once determined, for calculating the hydrogen ion concentration of any solution of the acid, at the given temperature. However, ionization constants of acids are not very accurately known; hence hydrogen ion concentrations are best determined directly, by one of the methods already discussed (§ 401), instead of being calculated from ionization constants. (Ex. 25–26.)

411. Buffer Salts

Review § 405. The concentrations with which we are dealing when we speak of *p*H are usually astonishingly small. For example, a solution that is just perceptibly acid to methyl red (*p*H = 5.0) contains 1 gram ion of H_3O^+ in 100,000 liters. That corresponds to a $N/100,000$ solution of an active acid. It is about the degree of acidity obtained by adding a single drop of concentrated hydrochloric acid to 20 gallons of water! A solution that is just perceptibly alkaline to phenolphthalein (*p*H = 9.0) contains only 1 gram ion of H_3O^+ in 1,000,000,000 liters, and 1 gram ion of OH^- in 100,000 liters. That corresponds to a $N/100,000$ solution of sodium hydroxide.

Solutions of such extreme dilution are very hard to preserve with any definite *p*H. If they are faintly acid they may be gradually neutralized by alkali dissolved from a glass container. If they are alkaline they are soon neutralized or even made faintly acid by carbonic acid derived from the carbon dioxide of the atmosphere. Distilled water that has been exposed to the air is likely to have a *p*H between 5 and 6, instead of 7, the value corresponding to exact neutrality.

The remedy for *unstable and inconstant pH* is to make up the solution by dissolving *not only an acid or alkali but also a salt or a mixture of salts*. This mixture will serve to hold the *p*H of the solution very nearly constant in spite of the addition of moderate mounts of additional acid or alkali. Mixtures that can thus stabilize *p*H are called *buffer mixtures*.

To serve as a buffer, a salt must be derived from a *slightly active acid* or a *slightly active base.* Salts (NaCl and K_2SO_4, for example) that happen to be derived from an acid and base *both of which are active* are *not serviceable as buffers.*

To show how buffer mixtures act let us imagine a solution containing both acetic acid and an acetate salt (*i.e.*, the acetate ion, $C_2H_3O_2^-$). We then have the equilibrium

$$\underset{\text{Acetic acid molecules}}{HC_2H_3O_2} + H_2O \underset{(b)}{\overset{(a)}{\rightleftharpoons}} H_3O^+ + \underset{\text{Acetate ions}}{C_2H_3O_2^-}$$

If we add a small amount of alkali to this solution (thus *withdrawing* H_3O^+ in a reaction in which this neutralizes alkali), reaction (*a*) immediately makes good the loss by producing more H_3O^+ from the reserve supply of acetic acid molecules.

On the contrary, if we add a small amount of acid (thus *increasing* the concentration of H_3O^+), the increase is immediately very nearly all withdrawn in reaction (*b*), which draws upon the reserve supply of acetate ions. So the *p*H of an acid solution that is buffered with an acetate salt remains very nearly constant in spite of the addition of moderate amounts of either acid or alkali.

It is easy to see that *buffering will be most effective against both alkali and acid if the reserve supply of acetic acid molecules*, to be used in reaction (*a*), *is equal to the reserve supply of acetate ions*, to be used in reaction (*b*); that is, $[HC_2H_3O_2] = [C_2H_3O_2^-]$. Substituting either of these two equal quantities for the other in the ionization constant for acetic acid,

$$K_a = \frac{[H_3O^+] \times [C_2H_3O_2}{[HC_2H_3O_2]}$$

the substituted quantity cancels out and we have $[H_3O^+] = K_a$. Take the logarithm of each side of this equation and reverse signs. Then we have $pH = pK_a$.

So we reach an important practical conclusion: *A salt derived from an active base and a slightly active acid will buffer most effectively in a solution whose pH is the* pK_a (§ 409) of the acid.

For example, the ionization constant of acetic acid (Appendix I) is 1.86×10^{-5}. The logarithm of this number is the sum of the logarithms of its two factors, namely $0.27 + (-5) = -(4.73)$. Reversing the sign we find 4.73 for the *p*H at which sodium acetate or potassium acetate will buffer most effectively. So we dissolve any

convenient amount of the acetate (perhaps enough to make a normal solution). We shall find this solution to be slightly alkaline because of hydrolysis (§ 397). By adding acetic acid (or, indeed, *any acid*) we can make it slightly acid, corresponding to a pH of around 4.7 (as judged by the color of some indicator). The solution will then be *well buffered* and *will tend to retain its initial pH in spite of the addition of moderate amounts of either alkali or acid.*

To buffer solutions in the alkaline range (pH greater than 7) we shall need the salt of *a slightly active base* and *an active acid.* Such a salt will buffer most effectively in a solution for which $[OH^-] = K_b$, the ionization constant of the base. Tables have been prepared that show what concentrations of acids, alkalies, and salts in buffered solutions will give definite, equally spaced, values of pH, over the ranges encountered in ordinary work. (Ex. 27–29.)

412. Buffer Salts in Nature and Industry

Buffer salts play a very important role in nature. Most of the juices of ordinary fruits and vegetables have a definite, though slight, acidity, which is held very nearly constant by the action of buffer salts. The blood has a definite, though very faint, alkalinity (pH, 7.33) which it maintains with the greatest precision, in part through the action of buffer salts.

Milk is buffered to a definite faint alkalinity and therefore remains for a long time uncurdled by the bacteria that convert milk sugar into lactic acid. Digestion is carried out in solutions buffered by organic salts contained in the digestive fluids. Indeed, all the processes of life, in plants and animals alike, take place in solutions that are buffered to the hydrogen ion concentration in which the chemical changes that those particular living cells are designed to accomplish take place most effectively.

Faint acidity, properly buffered, may be used to supplement heat in sterilizing solutions. Pure cultures of acid-resisting strains of yeast are now cultivated on a large scale in solutions buffered to a definite acidity, to discourage the growth of bacteria, while permitting the growth of yeast. Organic and inorganic salts in the soil tend to buffer different types of soil to different pH values, which may be suited to the growth of different crops. The amount of lime that must be applied to overcome the acidity of a soil therefore depends not so much on the pH of the soil as on the nature and amounts of the buffering salts in the soil.

Buffer salts are of frequent application in analytical chemistry.

For example, a solution that is $0.1N$ with acetic acid may be too actively acid for a given purpose. We therefore add sodium acetate or ammonium acetate to reduce the hydrogen ion activity, perhaps to that corresponding to $0.0001N$ acetic acid. Then all is well. We have the low hydrogen ion activity that we desire, and moreover we have a good supply of acid in reserve, as $HC_2H_3O_2$ molecules, to be drawn upon as needed, in any reaction in which protons disappear. To reduce the acidity of $0.1N$ acetic acid by *diluting* it to $0.001N$ or by partially neutralizing it with alkali would not serve, for we would then have no appreciable store of acid in reserve.

413. Acid-Base Pairs

In the reversible reaction

$$\underset{\text{Acid}}{\mathrm{HX}} \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \underset{\text{Base}}{\mathrm{X^-}} + \mathrm{H^+}$$

the substance HX is an acid, since it yields a proton to something else in the forward reaction, (*a*); whereas the ion X^- is a base, since it gains a proton from something else in the reverse reaction, (*b*). So, in general, *any substance formed reversibly from an acid by the loss of a proton is to be regarded as a base.* If the acid is strong (active), that is, has a decided tendency to lose protons, the base is correspondingly weak (slightly active), and conversely. Whenever an acid and base are so related that each is derived from the other by the gain or loss of a proton, each is called the *conjugate* of the other.

In the table on pp. 468, 469 are a number of acids, arranged in the order of *decreasing strength*, which is the same as the order of their conjugate bases, arranged in the order of increasing strength. The strongest acids are those nearest the top of the first column, whereas the strongest bases are those nearest the bottom of the second column. Some additional columns include a few bases that may be used as solvents, and some organic bases (all in the proper positions to show their approximate strengths in comparison with the bases in the second column).

Water is sometimes said to be *amphoteric* [5]—a word used to describe any substance that may function either as an acid or as a base. When water functions as an *acid* its conjugate base is hydroxyl ion:

$$\underset{\substack{\text{Acid} \\ pK_a\,=\,14}}{\mathrm{H_2O}} \rightleftharpoons \underset{\substack{\text{Base} \\ pK_b\,=\,0}}{\mathrm{OH^-}} + \mathrm{H^+}$$

[5] The term *amphiprotic* (p. 475) has nearly the same meaning.

THE BEHAVIOR OF ACIDS AND BASES IN THE PRESENCE OF DIFFERENT SOLVENTS

The most active acids are nearest the top in the left-hand column; the most active bases are nearest the bottom in the other columns.

pK_a	Acids		Conjugate Bases	Solvents (Acting as Bases)	Organic Bases	pK_a
				Hydrocarbons		
	HCl	⇌	$Cl^- + H^+$			
	$C_6H_5SO_3H$ Benzene sulfonic acid	⇌	$C_6H_5SO_3^- + H^+$	**HCOOH** Formic acid	$(C_6H_5^-)_3N$ Triphenylamine	
	$HClO_4$	⇌	$ClO_4^- + H^+$	**CH_3COOH** Acetic acid	CH_3CONH_2 Acetamide	−0.51
					$CO(NH_2)_2$ Urea	−0.18
0	H_3O^+	⇌	**H_2O** $+ H^+$ Water, acting as a base	**H_2O**		
0.4	H_2SO_4	⇌	$HSO_4^- + H^+$			
	$Al(H_2O)^{+++}$	⇌	$Al(OH)^{++} + H^+$		$C_6H_5NHCOCH_3$ Acetanilide	0.61
0.7	CCl_3COOH Trichloro-acetic acid	⇌	$CCl_3COO^- + H^+$			
1.77	H_2SO_3	⇌	$HSO_3^- + H^+$			
1.90	H_3PO_4	⇌	$H_2PO_4^- + H^+$			
2.00		(Thymol blue)				
3.14	HF	⇌	$F^- + H^+$			
3.65		(Methyl orange)				
4.73	$HC_2H_3O_2$ Acetic acid	⇌	$C_2H_3O_2^- + H^+$		$C_6H_5NH_2$ Aniline	4.66
5.0		(Methyl red)				
5.3	HSO_3^-	⇌	$SO_3^{--} + H^+$		C_5H_5N Pyridine	5.26
	$Mg(H_2O)^{++}$	⇌	$Mg(OH)^+ + H^+$			
6.5	H_2CO_3	⇌	$HCO_3^- + H^+$			
6.7	$H_2PO_4^-$	⇌	$HPO_4^{--} + H^+$			
7.0		(Neutral red)			$C_{21}H_{22}O_4N_2$ Strychnine	7.0
7.04	H_2S	⇌	$HS^- + H^+$			
8.0		(Cresol red)				
8.8		(Thymol blue, alk. range)				
9.0		(Phenolphthalein)				

or reactivity as acids ↑

or reactivity as bases

pK_a	Acid		Base	Solvent	Organic base	pK_a
9.2	H_3BO_3	$\rightleftharpoons$	$H_2BO_3^- + H^+$			
9.26	$NH_4^+ + H_2O$	$\rightleftharpoons$	$NH_4OH + H^+$		$(CH_3)_3N$ Trimethylamine	9.87
9.89	C_6H_5OH Phenol	$\rightleftharpoons$	$C_6H_5O^- + H^+$			
10.22	HCO_3^-	$\rightleftharpoons$	$CO_3^{--} + H^+$			
	$Ag(H_2O)^+$	$\rightleftharpoons$	$Ag(OH) + H^+$		$C_2H_5NH_2$ Ethylamine	10.75
					$C_{23}H_{26}O_4N_2$ Brucine	10.86
					$(C_2H_5)_2NH$ Diethylamine	11.1
12.1	(Nitramin)					
12.44	HPO_4^{--}	$\rightleftharpoons$	$PO_4^{---} + H^+$			
14.	**H_2O** Water, acting as an acid	$\rightleftharpoons$	$OH^- + H^+$			
14.9	HS^-	$\rightleftharpoons$	$S^{--} + H^+$			
				NH_3 (liquid)		
	NH_3	$\rightleftharpoons$	$NH_2^- + H^+$			
	OH^-	$\rightleftharpoons$	$O^{--} + H^+$			
	Hydrocarbons	$\rightleftharpoons$	Hydrocarbon radicals $+ H^+$			

Order of increasing strength (left side, acids; right side, bases)

In the left-hand portion of this table are listed a number of important acids, with their conjugate bases, in the order of decreasing strength (which is measured by the acid index, pK_a, whenever the solvent is water). Entries in parentheses show the relative strengths of a few indicators, treated as acids. Several hydrated cations are represented by arbitrary formulas, $Mg(H_2O)^{++}$, etc., and positions are assigned them that very roughly indicate their relative strengths as acids, hence relative tendency toward hydrolysis.

Solvents, acting as bases, and a few organic bases, are given places in the table at levels which indicate their strengths in comparison with the conjugates of the listed acids. If the activity constant of a base, expressed in the usual way (§ 409), is pK_b, that of the conjugate acid, when water is the solvent, and hence the place of the conjugate pair in the table, is $14 - pK_b = pK_a$.

The positions of pure solvents in the table can be given only approximately, because of difficulties in determining their effective concentrations when serving as solvents in comparison with their effective concentrations when dissolved in water.

When water functions as a *base* its conjugate acid is oxonium ion:

$$\underset{\substack{\text{Acid} \\ pK_a = 0}}{H_3O^+} \rightleftharpoons \underset{\substack{\text{Base} \\ pK_b = 14}}{H_2O} + H^+$$

It will be interesting to observe the positions of these two conjugate pairs in the table on pp. 468 and 469. It will be seen that water is not only a very weak acid but also a very weak base.

414. The Leveling Effect of an Active Solvent

Whenever a solvent can act as an acid or base it may react with substances dissolved in it and greatly alter their activity:

1. If the solvent can act as a base, gaining a proton, to form what we shall call a *solvent cation*,

$$\underset{\text{Solvent}}{H_2O} + H^+ \rightleftharpoons \underset{\substack{\text{Solvent} \\ \text{cation}}}{H_3O^+}$$

then all the strongest acids, on being dissolved, will yield protons to the solvent and be converted into the solvent cation. For example, hydrogen chloride, benzene sulfonic acid, and perchloric acid (the strongest acids listed on p. 468), on being dissolved in water, yield proton to the water and are converted into oxonium ion, H_3O^+. No wonder, then, that these acids, in solution in water, appear to be equally strong! They all suffer a loss in reactivity, in reacting with water, and are *leveled down* to the reactivity of H_3O^+, for which $pK_a = 0$. Our table suggests and experiment confirms that titration in a solvent having no very great tendency to act as a base will reveal differences in strength or reactivity among acids that appear to be equally strong when dissolved in water. Hydrogen chloride turns out to be much more active than perchloric acid, when titrated in formic acid as a solvent.

2. Conversely, if the solvent can act as an *acid*, losing a proton, to form a *solvent anion*,

$$\underset{\text{Solvent}}{H_2O} \rightleftharpoons \underset{\text{Solvent anion}}{OH^-} + H^+$$

then all the most active bases, on being dissolved, will gain protons from the solvent and will be converted into the solvent anion. Our table shows that the most active bases (O^{--} and NH_2^-), by reacting with water, are converted into OH^-, and so appear to be equally strong.

The transfer of protons to or from the solvent, as just described, is an example of *solvolysis* (*hydrolysis*, when the solvent is water). We have just seen that this process is practically complete when the most active acids are dissolved in a solvent that can act as a base or when the most active bases are dissolved in a solvent that can act as an acid.

415. Titration in Different Solvents

Our table enables us to determine which solvents will prove satisfactory in titrating an acid by a base, and what indicators will serve. If the solvent is *inert* (*i.e.*, serves neither as an acid nor a base) the titration involves three different acid-base pairs:

$$\textbf{Acid titrated} \rightleftharpoons \text{Its conjugate base} + H^+$$

$$\text{Indicator acid} \rightleftharpoons \text{Its conjugate base} + H^+$$

$$\text{Conjugate acid of base titrated} \rightleftharpoons \textbf{Base titrated} + H^+$$

If the neutralization of the acid by the base is to be reasonably *complete* these three pairs must appear in the table in the order here indicated, and several units of pK_a should intervene between the first and the last of them. If the end point is to be reasonably sharp an indicator must be used whose end point is at a pH that may be found by averaging the pK_a values of acid and base titrated. Then the acid titrated will be practically completely neutralized by the base titrated before the indicator begins to be affected; but the very next drop of added acid or base solution will neutralize the indicator base or acid, and change its color.

For example, someone proposes to titrate urea with acetic acid in an inert solvent. We look them up in the table and discover that they occur in the wrong order, the base titrated (urea) being higher in the table than the acid titrated (acetic acid). So the reaction between them will be far from complete, in any solvent. But if the acetic acid is replaced by one of the most active acids, say by hydrogen chloride, dissolved in an inert solvent, the acid and base titrated will occupy the proper relative positions in the table, and the reaction should be at least fairly complete.

If instead of an inert solvent we use one that reacts as a base, we must remember that it will react with the acid titrated and level this down to about its own position in the table. So hydrogen chloride, in the presence of water, drops down to the position $pK_a = 0$, and is no longer serviceable for neutralizing urea. Similarly, a solvent that reacts as an acid will bring any base titrated to its own position in the table.

We now propose to neutralize pyridine by trichloroacetic acid, in water as a solvent. We see that they have the proper relative positions in the table and are spaced several units apart. The water will not interfere, for it is a much weaker acid than trichloroacetic acid and a much weaker base than pyridine. So the titration should be successful. To select an indicator we average the pK_a values (0.7 for trichloroacetic acid; 5.26 for pyridine) and conclude that an indicator which has an end point at a pH of 3 should serve. We turn to the table on p. 458 and select tropeolin 00 for the indicator.

As a final example, we propose to titrate a monohydrogen phosphate (namely, the ion HPO_4^{--}) by acetic acid, in pyridine as a solvent. We immediately notice that this is a basic solvent, which reacts with the acetic acid and levels the latter down to its own position ($pK_a = 5.26$, in the table). That makes the subsequent reaction with the monohydrogen phosphate much less complete than it otherwise would be. If we use some solvent that is a weaker base than HPO_4^{--} and a weaker acid than acetic acid, the titration should be successful. Acetone or alcohol or even water will serve. Averaging the pK_a values (4.73 for acetic acid; 6.7 for the conjugate acid of HPO_4^{--}) we obtain 5.7 for the pH at which the indicator chosen should change color. In the table on p. 458 we find that chlorophenol red should be a satisfactory indicator. (Ex. 30, 31.)

416. The Electronic Theory of Acids and Bases

Though the most familiar acids contain hydrogen, there are numerous substances, *not containing hydrogen*, which have acid properties in the sense that they can react with and neutralize bases and change the color of indicators. To show that this is so, it is necessary to use some inert solvent, such as chloroform, instead of water. Crystal violet makes a suitable indicator.

Then we may titrate, in a solution in chloroform, using crystal violet as an indicator, the following substances (which are recognized as acids)

$$SO_2 \qquad SbCl_3 \qquad SnCl_4 \qquad HgCl_2$$

against the following substances (which are recognized as bases):

Aniline, camphor, dioxane, ether, and many other organic substances containing oxygen or nitrogen, and sometimes sulfur or arsenic.

In seeking an explanation of these interesting facts, G. N. Lewis (1916) observed that the base in every instance had a pair of unused electrons which it could donate to the acid, thus establishing a coordinate bond (§ 250) between the two molecules. This is also true of

reactions in which acids, in the ordinary sense of *proton donors*, neutralize ordinary bases:

$$\underset{\text{Oxonium ion}}{\left[\begin{array}{c} H:\overset{..}{O}:H \\ \overset{..}{H} \end{array}\right]^{+}} + \underset{\text{Hydroxyl ion}}{\left[:\overset{..}{\underset{..}{O}}:H\right]^{-}} \rightarrow \underset{\text{Water}}{\begin{array}{c} H:\overset{..}{O}:H:\overset{..}{O}: \\ \;\;\overset{..}{H}\qquad\overset{..}{H} \end{array}}$$

The product of the reaction just given is a doubled molecule of an associated solvent, water. If this is broken down into two simple molecules we see that the net result of the direct union, followed by decomposition, has been the *transfer* of a proton from H_3O^+ to OH^-. Whenever we have encountered the transfer of protons from acid to base, in the earlier pages of this chapter, the reaction was probably accomplished by the base first donating a pair of electrons to establish a bond with the acid. The compound thus formed then broke down in such a way as to accomplish a transfer of a proton from the acid to the base.

So, according to the Lewis or electronic theory of acids and bases, a *base* is any substance that has a pair of electrons which it can donate in establishing a coordinate bond with an electron-pair acceptor, or *acid*.

This theory is an improvement over previous views of the nature of acids and bases in that it recognizes that the transfer of protons is only an incident to a more general phenomenon, namely the ability of some atoms to lend electron pairs in establishing a bond with others. Yet its very generality tends to make this theory unusable, and particularly to make it unsuited to the instruction of beginners. The substances recognized as "bases" are compounds or ions of elements in the upper right-hand part of the Periodic Table, and are the same as those recognized as bases by the proton-transfer theory of neutralization. But the term acid is broadened past recognition, since most of the elements, with the exception of the inert gases and the first three halogens, can act as electron-pair acceptors, hence would be recognized as acids under the electronic theory.

Moreover we are not always sure whether the atoms in certain compounds are linked by coordinate bonds or in some other way. To accept the electron theory without reservation would be to obscure the boundaries of the rather clear-cut groups of substances that are now recognized as acids and bases. The beginner, at least, might end by failing to recognize that sodium hydroxide is a typical base by whatever theory.

For a review of this chapter, see Exercises 32–45.

A COMPARISON

Proton Transfer
(Protolysis)
Table of acid exponents, p. 468.

Order of increasing activity of acids ↑

$$\underset{\text{Acid}_1}{A} \rightleftharpoons \underset{\text{Base}_1}{B} + H^+$$

$$H_3O^+ \rightleftharpoons H_2O + H^+$$

$$\underset{\text{Acid}_2}{A'} \rightleftharpoons \underset{\text{Base}_2}{B'} + H^+$$

Order of increasing activity of bases ↓

Strongest acids are at top of left-hand column.

Strongest bases are at bottom of right-hand column.

The acid must occupy a higher position in the column of acids than the base does in the column of bases, if neutralization is to be complete.

Tendency toward protolysis (in the presence of water) is measured by the acid index (pK_a).

Water, acting as a solvent *base*, in equilibrium with H_3O^+ (in unit effective concentration) is arbitrarily assigned an acid index (pK_a) of zero.

When several different acids compete for a base, or conversely, they are neutralized successively, beginning with the strongest.

An acid-base indicator must have an acid index intermediate between values for the titrated acid and base.

Stronger acids than H_3O^+ (those above H_3O^+, in the table) transfer H^+ to water, practically completely (complete ionization); those farther and farther below H_3O^+ do so less nearly completely (incomplete ionization).

Stronger bases than H_2O (those below H_2O in the table) react with strong acids (namely, with H_3O^+) nearly completely.

Water reacts as a base, with strong or moderately strong acids; and as an acid, with strong or moderately strong bases. This is *hydrolysis*.

Electron Transfer
(Oxidation-Reduction)
Table of oxidation potentials, p. 313.

Order of increasing activity of reductants ↑

$$\underset{\text{Reductant}}{A} \rightleftharpoons \underset{\text{Oxidized Product}}{B} + e$$

$$H_2 \rightleftharpoons 2H^+ + 2e$$

$$\underset{\text{Reduced Product}}{A'} \rightleftharpoons \underset{\text{Oxidant}}{B'} + e$$

Order of increasing activity of oxidants ↓

Strongest reductants are at top of left-hand column.

Strongest oxidants are at bottom of right-hand column.

The reductant must occupy a higher position in the column of reductants than the oxidant does in the column of oxidants, if oxidation-reduction is to be complete.

Tendency toward oxidation-reduction (in the presence of water) is measured by the oxidation-reduction potential ($E°$).

Proton (in unit effective concentration), acting as an *oxidant* in equilibrium with hydrogen gas (under 1 atmosphere effective pressure) is arbitrarily assigned an oxidation potential of zero.

When several different reductants compete for an oxidant, or conversely, they are reduced or oxidized successively, beginning with the strongest.

An oxidation-reduction indicator must have an oxidation-reduction potential intermediate between values for the reductant and oxidant.

Metals above hydrogen in the table displace hydrogen from acids, nearly completely. Metals below hydrogen ordinarily do not displace hydrogen from acids.

Oxidants below H^+ in the table are readily and completely reduced by hydrogen gas (at least in the presence of an effective catalyst, such as platinum black).

Hydrogen accepts electrons from the most active reductants, such as metallic sodium, forming H^- (§ 530); and yields electrons to oxidants (presence of a suitable catalyst), forming H^+.

There are some important differences between proton transfer and electron transfer; for example, electron transfer often requires time for its accomplishment, or may fail to take place except in the presence of a catalyst. Moreover, loss and gain of electrons may take place in separate vessels. A great many reactions, for example the reduction of a permanganate, MnO_4^-, to a manganous salt, Mn^{++}, involve both proton transfer and electron transfer (§ 265).

Technical Words

Hydrolysis (two meanings), p. 447. **Titration,** p. 452.

Oxy-salt, hydroxy-salt—one intermediate in composition between an ordinary "normal" salt and an oxide or hydroxide.

Hydrogen electrode, p. 454. **Normal calomel electrode,** p. 454.

Ion-product, p. 456. ***p*H** or **hydrogen ion index,** p. 456.

Indicator, p. 457. **Acid-base indicator,** p. 457.

Potential (of an electrode), p. 614.

Acid or **base exponent** (pK_a or pK_b), p. 463.

Buffer mixture, p. 464. **Conjugate acid** or **base,** p. 467.

Amphoteric substance, p. 467. **Solvolysis,** p. 471.

Solvent cation or **anion**—an ion formed when a solvent molecule gains or loses a proton.

Ionization constant—the equilibrium constant of a reaction in which a substance reacts with a solvent, producing ions. The activity of the solvent is ordinarily taken as unity, in the expression for the ionization constant.

Leveling effect—a reaction (solvolysis) between a solvent and a dissolved acid or base, whereby the latter is converted into a substance that is decidedly less active as an acid or base.

Amphiprotic substance—one that may either gain or lose protons.

Exercises

1. Write an equation for the hydrolysis of magnesium acetate, in such a manner as to identify the products of the reaction, without attempting to show which ions are really concerned in it.

2. In the reaction of the preceding exercise both ions of the salt are separately concerned in the hydrolysis. Write an equation to show what happens to each of them. (These reactions are reversible.)

3. The corrosion of metals by sea water (containing chiefly salts of Na^+, K^+, Mg^{++}) is partly due to the fact that the ions of the dissolved salts render sea water a good conductor of electricity (details in § 504). What other cause of corrosion by sea water is suggested by an equation in § 396?

4. Predict what reaction a solution of each of the following salts will have toward most indicators, and why: sodium sulfate, sodium sulfide, ammonium nitrate, magnesium sulfate, zinc sulfate, potassium chloride, sodium cyanide, sodium acid sulfate, potassium fluoride.

5. Silver nitrate, when pure, dissolves in water to form a neutral solution. Is this behavior like or different from that of most other heavy metal nitrates?

6. There are three different sodium phosphates, with the respective formulas NaH_2PO_4, Na_2HPO_4, Na_3PO_4. Refer to the table on p. 449 to show that these formulas are those to be expected from the ions concerned.

7. Of the three salts mentioned in the preceding exercise, which is acid, which slightly alkaline, and which very alkaline toward phenolphthalein?

8. A student complains that a solution of the chloride of a heavy metal separates a precipitate on standing a few hours. What may the precipitate be, and how may its formation probably be prevented?

9. Crystalline aluminum chloride hydrate, $Al_2Cl_6 \cdot 12H_2O$, is prepared by evapo-

rating a solution of aluminum chloride in a current of hydrogen chloride gas. Explain the purpose of the latter.

10. When sodium chloride is strongly heated in a current of superheated steam, it is partially converted into sodium hydroxide. Write an equation in which this reaction is made to appear as a case of hydrolysis. Explain (§ 338) why a *current* of steam gradually brings about hydrolysis, in spite of the fact that neither of the two ions of sodium chloride is ordinarily subject to hydrolysis.

11. A student attempts to prepare crystals of ferric nitrate by evaporating a solution of this salt. The product obtained turns out to be insoluble in water, in spite of the fact that all "normal" nitrates are soluble. Explain what probably occurred and how this difficulty might have been avoided.

12. Distinguish between hydrolysis and hydration.

13. Explain why zinc chloride solutions are corrosive to metals.

14. In titrating an acid by an alkali, 64 ml of the acid solution required 40 ml of $N/5$ alkali. How many milliequivalents of each substance were present? What was the normality of the acid? 800, 125

15. If 50 ml of $N/5$ alkali are added to 50 ml of $N/4$ acid, how many milliequivalents of acid remain unneutralized? What volume of $N/5$ alkali will be needed to complete the titration? 250, 125

16. What actual weight of oxonium ion, H_3O^+, is found in 1 million liters of water, at 25°C? 1.9×

17. If the hydrogen ion concentration of an acid solution is 10^{-3} at 25°C, what is its hydroxyl ion concentration?

18. What is the pH of a solution having a hydrogen ion concentration of 2×10^{-3}? (Log 2 = 0.3.) 270

19. What is the hydrogen ion concentration of a solution whose pH is 9.4? (Log 4 = 0.6.) 4×

20. Within what range will methyl red serve as an indicator of the pH of a solution? Is this on the acid or on the alkaline side of the neutral point? Answer the same questions for phenolphthalein.

21. Write equations to represent the three successive stages in the reaction of phosphoric acid with water.

22. Choose an indicator for each of the following titrations:

Acetic acid and potassium hydroxide.
Hydrofluoric acid and sodium hydroxide.
Hydrochloric acid and calcium hydroxide.
Hydrogen sulfide (first stage) and potassium hydroxide.
Hydrogen sulfide (second stage) and potassium hydroxide.
Sulfuric acid (second stage) and ammonium hydroxide.

23. Look up the ionization constant of nitrous acid, then find its pK_a.

24. In a normal solution of a weak acid, HX, the acid is 0.01 per cent ionized What is the concentration of each ion, in gram ions per liter? What is the ionization constant? 10^{-4}, 10^{-8}

25. The ionization constant of a certain acid is 10^{-6}. Compare with the preceding problem to infer the hydrogen ion concentration of a normal solution of the acid.

26. What is the percentage ionization of the acid just considered, in a normal solution?

27. To what pH will KNO_2 buffer a solution? What must be added to a solution of KNO_2 to bring it to this pH?

28. With the aid of the table of ionization constants for acids, Appendix I, select two sodium salts that will serve as effective buffers in a solution with a pH of about 6.5 to 6.7. What must be added to each salt solution to bring it to the specified pH?

29. What is the pK of an acid whose sodium salt serves as a buffer in a solution whose pH is 9.2? Name such a salt.

30. Will phenol (serving as an acid) react reasonably completely with carbonates (namely, with CO_3^{--})? Will it react with strong alkalies? Suggest an indicator for the latter reaction.

31. Is the reaction of boric acid with ammonium hydroxide complete or incomplete?

32. A $N/10$ solution of HCl conducts about 100 times as well as a $N/10$ solution of acetic acid. Explain.

33. From what has the concentration of the ions in water been inferred?

34. If the temperature is increased does water become a better or a worse conductor? Why?

35. What unit is used in expressing the hydrogen ion concentration or hydroxyl ion concentration of a solution?

36. Does the pH of a solution decrease or increase with increasing acidity?

37. If sodium acetate is added to water will the pH be above or below 7? Explain (§ 397).

38. A student suggests that because two solutions have the same pH, equal volumes will require the same volume of $N/10$ alkali to neutralize them. Defend or criticize this suggestion.

39. Write a paragraph explaining how the pH of a solution may be determined with the aid of an indicator.

40. In determining the pH of a solution the comparison solution never contains acid or alkali alone, but one of these, supplemented by a salt. Why?

41. A measurement of the conductivity of a $N/10$ acid indicates that both the ions of the acid must be present in a concentration of approximately 10^{-4} gram ion per liter. Roughly, what is the ionization constant of the acid?

42. By reference to a table of ionization constants select two acids that are more active and two that are less active than acetic acid.

43. Indicate some instances of buffered solutions in nature and industry.

44. How is a hydrogen electrode prepared? What is the purpose of the coating of platinum black?

45. In titrating an acid by a base, under what conditions will the pH rise suddenly through a very considerable range, at the end point of the titration?

Chapter 30

PRECIPITATION

417. Tests for Individual Ions

Individual cations and anions may be identified by *qualitative tests* that sometimes depend (1) on the color that the ion imparts to a flame, and sometimes (2) on the change in color that is observed when a *solution* containing the ion is treated with an appropriate reagent (usually an oxidizing or reducing agent). Other qualitative tests for individual ions depend (3) on the formation of a *precipitate* that happens to be readily identified by its color or other properties.

The list of slightly soluble ionic substances in § 288 offers suggestions for such "precipitation tests." It tells us, for example, that lead chromate is insoluble, and so suggests lead ion, Pb^{++}, as a test for a chromate and chromate ion, CrO_4^{--}, as a test for lead. If the ion tested for is really present we should obtain lead chromate, a lemon-yellow precipitate. *Most tests depending on the formation of a precipitate can be used as a test for either ion in the precipitate, when the other ion is added as a soluble ionic compound.*

In precipitation tests we must, of course, be careful to exclude any ions that tend to prevent the precipitation or that confuse the issue by being jointly precipitated with the ion to be detected. That is why textbooks of qualitative analysis describe elaborate procedures to get the cations pretty well separated from one another before making final tests for any of them. *It is rarely that a test for any ion is so characteristic that it may be made in the presence of almost anything else that may be present.*

When a precipitate has finally been obtained we nearly always need to perform some *confirmatory test* to make sure that it really is what it is supposed to be. A white crystalline precipitate, presumed to be calcium oxalate, may be some other oxalate, or calcium sulfate, or something else. If it really is calcium oxalate it should prove to be insoluble in dilute acetic acid but readily soluble in dilute hydrochloric

acid (forming a solution which when introduced into the base of a Bunsen flame imparts to the flame the brick-red color characteristic of calcium ion).

418. Effect of One Ionic Substance on the Solubility of Another

The solubility of a slightly soluble ionic substance is sometimes *increased* and sometimes *decreased* by the presence of another ionic substance. We can get an idea of why this is so if we consider the opposing processes:

$$\text{Ionic solid} + H_2O \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \text{Hydrated ions (in a saturated solution)}$$

The opposing reaction rates balance and we have equilibrium when the solution is saturated.

If we now add another ionic substance there are several possibilities:

1. *The added substance may furnish some ion already present in the saturated solution* (as when any soluble iodate is added to a saturated solution of silver iodate). By thus increasing the concentration of the ion (iodate) that is common to both substances we increase the rate at which the crystal lattice is rebuilt in reaction (*b*). Thus (*b*) for a little while predominates over (*a*), and the solubility of the original substance is *decreased.* This is often termed the "common-ion effect."

2. *The added substance always furnishes one or more ions not already present in the saturated solution.* These attract the oppositely charged ions in the crystal lattice and hence assist in reaction (*a*), in which the crystal lattice is torn down. The solubility of the original substance is thereby *increased.* This "electrostatic effect," sometimes called the "salt effect," is most pronounced when the ions originally present or later added are doubly or triply charged. It may then more than offset the common-ion effect.

Consider, for example, crystals of lead chloride in equilibrium with a saturated solution of that salt. Adding an excess of *either* lead ion or chloride ion tends to decrease the solubility of the lead chloride (common-ion effect). But in practice we must always add some foreign ion, too, since Pb^{++} has to be added as $Pb(NO_3)_2$ or some other lead salt, and Cl^- as NaCl or some other chloride. The foreign ion tends to increase the solubility (electrostatic effect). Actually, when lead nitrate is added to a saturated solution of lead chloride, the electrostatic effect predominates, and the solubility of the lead chloride is *increased.*

3. *The added ionic substance may combine with either or both of the hydrated cations or hydrated anions, converting them into something else.* Thus the concentration of either one or both of these ions is reduced almost to zero. In consequence, reaction (*b*), in the preceding equilibrium, practically ceases. But reaction (*a*) keeps on going until the ionic solid, in many instances, is completely dissolved (details in §§ 425, 426).

To summarize: When an ionic solid is in equilibrium with a saturated solution of the same substance the addition of a slight excess of either of its ions will diminish its solubility and cause some of it to be precipitated from solution (common-ion effect); but the addition of a slight amount of other ions will slightly increase its solubility (electrostatic effect). Whenever the added ion enters into a chemical reaction with either or both of the ions of the solid the solubility of the latter may be very greatly increased. (Ex. 1–4.)

419. Effective Concentration or Activity

The thoughtful reader must already have sensed that the laws of nature are usually not quite so simple as we pretend. We stated a number of simple laws (Avogadro, Boyle, Charles, Graham, Henry) for gases (§§ 31, 102, 104, 111, 290); then we had to admit that they apply only to an imaginary *ideal gas*, and that real gases depart from these simple laws, more and more widely as the temperature is lowered or the pressure increased.

We also stated a few simple laws governing the vapor pressure, freezing point, boiling point, and osmotic pressure of solutions (§§ 295, 296, 300); then we had to admit that they apply only to *ideal solutions*, and that real solutions depart from them, more and more widely as the solutions become more and more concentrated, particularly when the dissolved substance is ionic. So it has often been remarked that there is no simplicity in nature, but only in ourselves in expecting it.

If we ask why somewhat compressed gases and somewhat concentrated solutions deviate from the simple laws of rarefied gases or dilute solutions the answer is plain: *In rarefied gases or dilute solutions the gas molecules or solute molecules or ions are so far apart that they exert no appreciable attraction for one another* (§ *100*). But as a gas is cooled or compressed, or as a solution is made more concentrated, *intermolecular* or *interionic forces* appear, which are a restraining influence, and deprive the gas molecules or the dissolved molecules

or ions of the complete freedom of motion and independence of action that they have when widely separated from one another.

We can easily perceive some of the consequences of such restraining forces. In considering reaction rates we assumed that collisions between the reacting molecules or ions were entirely at random, and we concluded that the reaction rate should then be proportional to the concentration (or sometimes to the square or the cube of the concentration) of each reactant (§ 332). But if the concentration is very great, or if the reacting particles are electrically charged, the attractions or repulsions between them alter the frequency of their collision with one another, hence prevent the reaction rate from being what it would be in an ideal gas or solution of that concentration.

In a solution of an ionic substance the attraction between oppositely charged ions prevents them from being scattered through the solution at random; instead, *each kind of ion tends to become surrounded by those of opposite charge to itself.* As the solution becomes more and more concentrated this effect becomes more and more pronounced. It is carried to extremes in an ionic crystal, where each ion is surrounded by definite number of ions of opposite charge to itself, in a definite space pattern.

So we see that the actual *concentration* of a gas or solution is a reliable guide to escaping tendency or tendency toward reaction only when the concentration is very small. For cooled or compressed gases or fairly concentrated solutions (especially solutions of ionic substances) it is convenient to disregard the actual concentration and talk about the *effective concentration* or *activity*, which is the concentration that the gas or dissolved substance would need to have in the absence of disturbing forces [1] to behave as it actually does behave. By substituting effective concentration or activity for the actual concentration, the simple laws already studied may be applied even to compressed gases or concentrated solutions.

The effective concentration (*activity*) of a component of a solution or the effective pressure (*fugacity*) of a gas or vapor may be calculated *by comparing actually observed properties with properties observed when the concentration is greatly diminished.* The activity (in moles per liter) may always be expressed as the product of the actual concentration, c, and a corrective factor or *activity coefficient*, α (alpha).

[1] The disturbing forces here referred to are of course those acting between the molecules of a cooled or compressed gas, or between the molecules (and especially between the ions) of a dissolved substance.

The activity coefficient varies with the concentration, c. In an *ideal environment* activity and concentration are identical, hence $\alpha = 1$. In one less favorable than an ideal environment to the development of escaping tendency or reactive properties, α falls below 1. In a more favorable environment, it rises above 1. In $5N$ hydrochloric acid, for example, it is about 2.5, and for concentrated ($16N$) hydrochloric acid it is about 43. In other words, hydrochloric acid, in a concentrated solution, is about 43 times as active an acid as would be expected from its concentration, if we compare it with very dilute solutions of hydrochloric acid! A minimum activity coefficient ($\alpha = 0.76$) is found with a $0.5N$ solution of hydrochloric acid. With other active acids a similar effect is observed.

The equilibrium constant, K_a, expressed in terms of activities instead of in terms of concentrations, K_c, or partial pressures, K_p (§ 343), is rigidly constant for any given reaction at any given temperature, instead of being merely roughly constant. The logarithm of the activity coefficient is a measure of the decrease in *potential energy* as molecules or ions pass from an ideal environment to their actual environment. That makes the activity coefficient something more than a mere evasion for the purpose of bringing experimental observations into harmony with theories!

420. The Activity Product

We can calculate the actual decrease or increase in solubility whenever we know the activity (effective concentration) of each of the ions in the solution. Consider a slightly soluble ionic substance in equilibrium with a saturated solution:

$$\text{Ionic solid} + x\text{H}_2\text{O} \underset{(b)}{\overset{(a)}{\rightleftharpoons}} \underset{\substack{\text{Hydrated}\\\text{cation}}}{\text{Ctn}^+} + \underset{\substack{\text{Hydrated}\\\text{anion}}}{\text{An}^-}$$

The rate of the forward reaction (a), at equilibrium, is a *constant quantity*, depending on the temperature. The rate of the reverse reaction (b) is proportional to the product of the two activities (effective concentrations):

$$[\text{Ctn}^+] \times [\text{An}^-] \qquad \text{(See § 332)}$$

If equilibrium is to be maintained the two opposing reaction rates must be equal. That is,

$$[\text{Ctn}^+] \times [\text{An}^-] = \text{A constant for each temperature}$$

In other words: *Whenever a slightly soluble ionic substance is in equilibrium with a saturated solution, the product of the activities of its ions, at each temperature, has a constant value,* called the *activity product* (or, often, the *solubility product*).

Activity Products (20°C)

This table gives values of *pA* (the logarithm, with sign reversed, of the activity product) for each of a number of slightly soluble ionic compounds. Cations of the heavy metals are arranged in the order of increasing solubility of their sulfides.

	S^{--}	OH^-	F^-	Cl^-	Br^-	I^-	CO_3^{--}	$C_2O_4^{--}$	SO_4^{--}	CrO_4^{--}
Hg^{++}	53.5									
Hg_2^{++}	47.0			18.2	22.5					
Ag^+	50.0	7.7		10.0	12.6	16.0	11.3	11.3		11.7
Cu^+						11.3				
Cu^{++}	41.5									
Bi^{+++}	71.8									
Pb^{++}	27.5		8.15				13.5	10.5	8.0	13.75
Cd^{+++}	28.3									
Ni^{++}	27.0									
Co^{++}	26.7									
Zn^{++}	25.16									
Fe^{++}	18.4 to 21.6									
Mn^{++}	15.16 *									
Mg^{++}		10.9	8.16				3.7			4.07
Ca^{++}			10.46				7.9	8.7	4.2	
Sr^{++}							8.8	7.3	6.56	
Ba^{++}							8.16	6.77	10.0	8.7

* Pink form.

To find the solubility product corresponding to any value of *pA*, begin by expressing *pA* as a whole number *minus* a decimal fraction. Thus 8.16 is to be expressed as 9 − 0.84. This is the logarithm of the desired solubility product, but with sign reversed. The solubility product is therefore the number whose logarithm is + 0.84 − 9. It is 6.9×10^{-9}.

If two or more ions of any given kind appear in the equilibrium equation the activity of that ion must be raised to the corresponding power in finding the activity product. Thus for silver chromate, Ag_2CrO_4, the activity product is

$$[Ag^+]^2 \times [CrO_4^{--}]$$

Activity products may easily be calculated from solubilities, and conversely. For example, the solubility of calcium oxalate, at 20°C, is about 5.8×10^{-3} g/l. Dividing this by the formula weight (128) we

find that it is equivalent to 4.5×10^{-5} gram-formula weight per liter. So a saturated solution of calcium oxalate at 20°C contains 4.5×10^{-5} gram-formula weight of Ca^{++} and the same of $C_2O_4^{--}$, in each liter. In such very small concentrations, concentrations are not distinguishable from effective concentrations (activities). The activity product for calcium oxalate is therefore

$$[Ca^{++}] \times [C_2O_4^{--}] = (4.5 \times 10^{-5})^2 = 2.0 \times 10^{-9}$$

Activity products are conveniently indicated by the value of pA, their negative logarithm, in the table on p. 483. *Each unit increase in pA indicates a 10-fold decrease in the activity product,* or a $\sqrt{10}$-fold decrease in the solubility of such salts as AgCl and PbS (in which cations and anions are present in equal numbers). *The greater the value of pA the less the solubility of the substance, provided that we are comparing substances of the same formula type.* (Ex. 5–7.)

421. Conditions for Producing a Precipitate

To produce a precipitate, we must meet two conditions:

1. We must intermingle solutions of the necessary ions in such concentrations that the product of their activities (effective concentrations) *exceeds* the activity product of the precipitate at that temperature.

For example, we may wish to form a precipitate of calcium oxalate by adding a solution of a soluble oxalate to a solution of a calcium salt containing 0.1 gram-formula weight of Ca^{++} in each liter. Substituting 0.1 for Ca^{++} in the expression

$$[Ca^{++}] \times [C_2O_4^{--}] = 2 \times 10^{-9} \quad \text{(the activity product)}$$

we find

$$[C_2O_4^{--}] = 2 \times 10^{-8} \quad \text{gram-ion per liter}$$

Any concentration of $C_2O_4^{--}$ above this exceedingly slight value will cause precipitation of calcium oxalate to begin, *if we can prevent the solution from remaining supersaturated.*

2. We must often prevent supersaturation by "inoculating" the solution with a few crystals or even an unweighable trace of the precipitate to be formed. But in analytical chemistry some method other than inoculation must usually be resorted to. Sometimes precipitation begins if a supersaturated solution is violently shaken or if the walls of the vessel are rubbed. *A reasonable excess of the pre-*

cipitant aids in preventing supersaturation and causes precipitation to be more rapid, but may yield a precipitate so finely divided that it is difficult to filter. (Ex. 8–10.)

422. Crystalline vs. Amorphous Precipitates

Most apparently amorphous (non-crystalline) precipitates (silver chloride, for example) are shown by X-ray examination to consist of aggregates of crystalline particles of less than microscopic dimensions. Such materials are sometimes termed *cryptocrystalline.* Yet a few precipitates (hydrous ferric oxide, for example) seem to be truly amorphous when freshly precipitated.

Many precipitates can be obtained either as apparently amorphous jellies, flocculent deposits, fine crystals or coarse crystals, according to the conditions under which they are formed. When precipitation takes place from a solution that is extremely supersaturated (in other words, from a solution in which $[Ctn^{+}] \times [An^{-}]$ greatly exceeds the activity product for a saturated solution) collisions between oppositely charged ions within the solution instantly produce an enormous number of crystal nuclei. These have no time to grow, even to microscopic dimensions, before the supersaturation is reduced to zero. The precipitate is therefore flocculent or a jelly.

But when the solution from which precipitation occurs is only slightly supersaturated, a relatively small number of crystal nuclei are produced, which grow for a long time before the solution is reduced from supersaturation to saturation. The result is a crystalline precipitate. The lower the degree of supersaturation the fewer crystal nuclei are formed, the more slowly they increase in size, and the larger the resulting crystals.

There are still other factors that help to determine the nature of a precipitate. *Precipitates of complicated structure and low mechanical strength are most apt to be amorphous and to remain so.* The hydrous oxides, $Zn(OH)_2$, $Al(OH)_3$, $Fe(OH)_3$, etc., are gelatinous precipitates not merely because they are extremely insoluble, hence are always precipitated from solutions that are highly supersaturated with respect to the precipitate, but because they combine with water to form sponge-like structures, in which the cations are linked to one another through water molecules. The structure therefore has little mechanical strength or rigidity.

Crystals of microscopic dimensions are perceptibly more soluble than larger ones, the excess solubility being greatest for crystals that are mechani-

cally strong. The degree of supersaturation of a solution from which microscopic strong and hard crystals are being deposited is therefore distinctly less than one would infer from the solubility of coarsely powdered material. Barium sulfate and silver chloride have practically the same solubility when coarsely powdered. But the former is relatively strong and hard, hence it separates from a solution that is not so highly supersaturated as one depositing silver chloride. Barium sulfate therefore precipitates more slowly and is distinctly crystalline, whereas silver chloride is flocculent. Other factors, such as differences in ionic charge, doubtless contribute to the differences between these two precipitates.

423. Some Practical Conclusions

From what precedes we can draw some useful practical conclusions: Since most salts are more soluble in hot water than in cold, precipitation is ordinarily carried out in a hot solution. Then the degree of supersaturation during the formation of the precipitate is less than it otherwise would be, and the tendency is to form large crystals, readily filtered. The higher temperature also aids the regrouping of haphazardly arranged crystal nuclei in an apparently amorphous or *cryptocrystalline* precipitate (p. 492), to form a denser and less soluble crystalline product. Furthermore, a precipitate separating from a hot solution is usually less contaminated with foreign materials, either *coprecipitated* or else *adsorbed* (§ 328) on its surface.

Any other means for producing a precipitate that separates slowly, from a solution not too greatly supersaturated, will aid in securing a readily filterable precipitate. For example, the precipitation of calcium oxalate may be begun in a hot, somewhat acid solution, in which this salt is much more soluble than in pure water. Then the acid is very slowly neutralized by the addition of a dilute solution of ammonium hydroxide.

Sometimes two solutions which are to react to produce a precipitate are added, simultaneously and very slowly, to hot water which is being violently stirred. Then the solution can never be very greatly supersaturated with respect to the precipitate, for $[Ctn^+] \times [An^-]$, within the solution, never greatly exceeds the activity product of the precipitate. The precipitate therefore forms slowly and is apt to be coarsely crystalline and readily filterable.

Whatever the conditions under which a precipitate may have been formed, one still needs to decide whether to filter it while the solution

is still hot, or after cooling. A hot solution filters much more rapidly, but many precipitates are so much more soluble at higher temperatures that the solution must be cooled before being filtered, if appreciable quantities of the substance are not to be lost by remaining dissolved.

A final word of caution: We have said that the precipitant (precipitating reagent) is always added *slowly*, while the solution is being vigorously stirred, in order that the supersaturation of the solution with respect to the precipitate may never be very great; yet a slight *excess* of the precipitant should be present in the end, since the solubility of an ionic precipitate is always greatly decreased by a slight excess of either of its ions (an application of the Principle of Mass Action, § 338). The ion that is *most effective* in reducing the solubility of the precipitate is the one that appears with the highest exponent in the expression for the activity constant. (Ex. 11–17.)

424. Order of Precipitation

Very often the addition of a reagent to a solution may precipitate *several different ions*. These do not precipitate together but one after another, in the order of increasing solubility of the precipitates concerned, provided that the precipitant is not added too rapidly, and that the solution does not remain supersaturated with respect to one or more of the precipitates.

For example, a solution contains a soluble chloride and a soluble chromate, namely, the ions Cl^- and CrO_4^{--}. The corresponding silver salts, $AgCl$ and Ag_2CrO_4, are both very slightly soluble. But the former is less soluble than the latter and so precipitates first. It may begin to precipitate (provided that the solution does not remain supersaturated) as soon as $[Ag^+] \times [Cl^-] = 10^{-10}$ (the activity product of silver chloride). If the initial concentration of Cl^- is 0.1 gram ion per liter we may substitute $[Cl^-] = 0.1$ in the expression just given and so find $[Ag^+] = 10^{-9}$ gram ion per liter as the least concentration of Ag^+ that can cause precipitation of $AgCl$ to begin.

As the precipitation of $AgCl$ (white) continues, $[Ag^+]$ must be increased in proportion as $[Cl^-]$ is diminished (by being removed by precipitation). When the added Ag^+ is just equal to the Cl^- originally present (so that neither ion is in excess) the concentration of each of these ions is the same as in a saturated solution of $AgCl$ in pure water, namely,

$$[Ag^+] = [Cl^-] = \sqrt{10^{-10}} = 10^{-5} \text{ gram ion per liter}$$

Thereafter, as a very little extra Ag^+ solution is added, the concentration of Ag^+ rises to a value at which Ag_2CrO_4 (a brick-red precipitate) begins to separate. This may happen when

$$[Ag^+]^2 \times [CrO_4^{--}] = 2 \times 10^{-12} \quad \text{(the activity product of silver chromate)}$$

If $[CrO_4^{--}] = 0.01$ gram ion per liter, we find that

$$[Ag^+] = \sqrt{2 \times 10^{-10}} = 1.4 \times 10^{-5} \text{ gram ion per liter}$$

is the least concentration of Ag^+ that can cause precipitation of Ag_2CrO_4 to begin. Actually, several times this concentration is needed to cause the formation of enough precipitate to be recognized by a visible red color.

The preceding calculations relate to the famous *Mohr method* for determining chloride ion by titration with a standard solution of silver nitrate. A 0.01 molar solution of sodium chromate is used as an indicator. A white precipitate of silver chloride is first formed. When its precipitation is complete (except for a negligible trace, remaining dissolved), the next slight excess of Ag^+ produces a red color, due to silver chromate, and so indicates that the titration is complete. (Ex. 18–20.)

425. Using an Acid to Dissolve a Precipitate

Consider a precipitate of calcium fluoride, in equilibrium with a saturated solution of that substance in water:

$$\underset{\text{Precipitated}}{CaF_2} + xH_2O \underset{(b)}{\overset{(a)}{\rightleftharpoons}} Ca^{++} \text{ (hydrated)} + 2F^- \text{ (hydrated)}$$

If we now add an acid to the solution, H^+ (from the acid) combines with F^- to form molecules of HF. Thus the concentration of fluoride ions in the solution is greatly reduced and reaction (*b*) is almost prevented. But reaction (*a*) keeps on going, introducing more Ca^{++} and F^- ions into the solution, until equilibrium is restored. The addition of an acid to the solution in equilibrium with the precipitated fluoride has greatly increased the solubility of the fluoride. The addition of enough acid will cause the precipitate to dissolve completely.

So, in general, addition of an active acid will usually cause a precipitate to dissolve, provided that the anion of the precipitate is derived from a *slightly active acid* (in other words, has a strong tendency to combine with H^+ to form an acid molecule). But if a precipitate is extremely insoluble or if its anion is derived from an active acid, addition of an acid will usually fail to dissolve it.

By adjusting the concentration of the added acid it is possible to dissolve the most readily soluble of a mixture of precipitates and leave the rest undissolved. Or by carrying out a precipitation in presence of a definite concentration of an active acid the least soluble of a group of precipitates may be thrown down, leaving the rest in solution. This is the principle used in the separation of sulfides of the heavy metals into two distinct groups, as described in § 307. (Ex. 21–24.)

426. Dissolving a Precipitate by forming a Complex Ion

Of course there are other ways of dissolving a precipitate than by adding an acid. In general, *a precipitate may be dissolved by anything that will transform one of the ions of the precipitate, sufficiently completely, into something else.*

For example, consider precipitated silver chloride, in equilibrium with a saturated solution of that substance in water, at 25°C:

$$AgCl \text{ (solid)} + xH_2O \underset{(b)}{\overset{(a)}{\rightleftharpoons}} Ag^+ \text{ (hydrated)} + Cl^- \text{ (hydrated)}$$

The activity product of silver chloride at 25°C is 10^{-10}. In other words $[Ag^+] \times [Cl^-] = 10^{-10}$ (gram ion per liter)^2. Since the two ion concentrations are equal, $[Ag^+] = [Cl^-] = \sqrt{10^{-10}} = 10^{-5}$ gram ion per liter.

Now let us add a solution of ammonium hydroxide. This reacts with the Ag^+ ions of the solution, transforming them into "complex ions":

$$Ag^+ + 4NH_4OH \rightleftharpoons \underset{\substack{\text{Diammine} \\ \text{silver ion}}}{Ag(NH_3)_2{}^+} + 4H_2O$$

Thus the concentration of Ag^+ in the solution is so greatly reduced that $[Ag^+] \times [Cl^-]$ becomes far less than the activity product, 10^{-10}. In other words, reaction (*b*), in the second preceding equation, no longer balances or offsets reaction (*a*). So (*a*) predominates for a time, bringing more Ag^+ and Cl^- into solution. The precipitate will dissolve completely if Ag^+ is so far decreased, by conversion into the complex ion, that $[Ag^+] \times [Cl^-]$ never again becomes equal to 10^{-10}, in spite of the greatly increased value of $[Cl^-]$ that is obtained if all the precipitate dissolves.

Let us assume, for example, that 0.01 gram-formula weight of AgCl is completely dissolved by being treated with NH_4OH, the solution then having a volume of 200 ml. If the precipitate all dissolves it

introduces 0.01 gram ion of Cl^- into 200 ml, hence $[Cl^-] = 5 \times 10^{-2}$ gram ion per liter. Substituting this in $[Ag^+] \times [Cl^-] = 10^{-10}$ we find $[Ag^+] = 2 \times 10^{-9}$ gram ion per liter. So the addition of NH_4OH must have reduced the concentration of Ag^+ below this extraordinarily low value, in order to make the precipitate dissolve completely!

427. More About Complex Ions

Any ion formed by the union of ordinary simple ions with one another or with electrically neutral molecules (other than molecules of water) is called a complex ion. Diammine silver ion, $Ag(NH_3)_2^+$, is an example of a group of complex cations called *ammines*. (Note the double *m*, to distinguish them from a group of organic compounds termed amines, § 464.) Ammines are formed by the union of various cations with (usually) 4 or 6 molecules of ammonia, NH_3. A salt, one or both of whose ions is complex, is called a *complex salt*. For example, when AgCl is dissolved by addition of NH_4OH the solution contains the ions $Ag(NH_3)_2^+$ and Cl^-, which are ions of the very soluble complex salt called diammine silver chloride, $Ag(NH_3)_2Cl$, also frequently written $AgCl \cdot 2NH_3$.

Some important groups of complex ions:

1. The ammines, just mentioned.

2. The complex cyanides, formed by the direct union of cyanide ions, CN^-, with various cations:

$$Ag^+ + 2CN^- \rightleftharpoons \underset{\text{Argenticyanide ion}}{Ag(CN)_2^-}$$

$$\underset{\text{Ferrous ion}}{Fe^{++}} + 6CN^- \rightleftharpoons \underset{\text{Ferrocyanide ion}}{Fe(CN)_6^{----}}$$

$$\underset{\text{Ferric ion}}{Fe^{+++}} + 6CN^- \rightleftharpoons \underset{\text{Ferricyanide ion}}{Fe(CN)_6^{---}}$$

3. Complex thiocyanates

$$Ag^+ + 2CNS^- \rightleftharpoons \underset{\text{Argentithiocyanate ion}}{Ag(CNS)_2^-}$$

4. Complex iodides:

$$Pb^{++} + 4I^- \rightleftharpoons \underset{\text{Plumbiiodide ion}}{PbI_4^{--}}$$

Observe that *the charge carried by the complex ion, in every instance, is the algebraic sum of the charges of the simple ions from which it is*

produced. All these groups of complex ions and a number of others are in common use as means for redissolving precipitates, in separating various precipitated substances from one another.

Every reaction producing a complex ion is reversible, though often only to a very slight degree. (Observe the double arrows of the preceding equations.) So each of these reactions has a definite equilibrium constant (§ 340), which is very easily determined. When the equilibrium constant (often called the *stability constant* of the complex ion) has a very large numerical value (10^{10} or 10^{20}, for example) we may conclude that the simple ions are converted into the complex ion, almost completely, by the indicated reagent.

The formation of such a complex ion is a very effective way of dissolving a precipitate containing a simple ion:

$$\underset{\substack{\text{Silver}\\\text{cyanide}\\\text{(precipitated)}}}{AgCN} + \underset{\substack{\text{Reagent:}\\\text{a soluble}\\\text{cyanide}}}{CN^-} \rightleftharpoons \underset{\substack{\text{Complex}\\\text{anion}\\\text{(dissolved)}}}{Ag(CN)_2^-}$$

(If the reagent, in this instance, is KCN the reaction produces the complex salt called potassium argenticyanide, $KAg(CN)_2$, which contains the complex anion just indicated.)

But a precipitate which happens to be extremely slightly soluble (hence has a very small activity product) may fail to be dissolved completely, even in forming a complex ion which has a high stability constant. For example, silver iodide is so much less soluble than silver chloride that it fails to be dissolved by ammonium hydroxide.

In closing our brief discussion of complex ions one more fact should be emphasized: *When a complex ion has a high stability constant* (in other words, when the reaction producing it is very nearly complete) *the concentration of one of the simple ions in equilibrium with the complex ion may be so greatly reduced that ordinary tests fail to detect the simple ion at all.*

For example, a solution of potassium ferricyanide, $K_3Fe(CN)_6$, fails to reveal the presence of iron by any of the ordinary tests, since practically all of it is present in the complex ferricyanide ion, $Fe(CN)_6^{---}$, and the concentration of the simple ion, Fe^{+++}, is almost zero. Whenever a simple ion is detectable in the presence of a complex ion produced from it we may be sure that its conversion into the complex ion is relatively incomplete; or else that the test for the simple ion is of extreme delicacy (perhaps because it produces a precipitate that is extremely slightly soluble). (Ex. 25–27.)

Technical Words

Confirmatory test, p. 478. **Activity,** p. 481.

Common-ion effect—the tendency that any ion has to decrease the solubility of any ionic substance containing it.

Electrostatic effect or **salt effect**—the tendency that any ion has to increase the solubility of any ionic substance that does not contain it.

Activity coefficient—a factor used to multiply the concentration to obtain the activity or effective concentration.

Activity product—the product of appropriate powers of the *activities* of the ions (1) in a saturated solution of an ionic substance (§ 420); (2) in a pure solvent (§ 404).

Solubility product—the product of the appropriate powers of the actual *concentrations* of the ions in a saturated solution of a slightly soluble salt. It approximates the activity product, just defined (case 1), and is indistinguishable from it when the salt concerned is but very slightly soluble and is composed only of univalent ions.

Cryptocrystalline—composed of crystals that are so small as to escape detection except by examination of the material with X-rays.

Complex ion—an ion produced by the direct union of simple ions with one another or with electrically neutral molecules.

Stability constant—the equilibrium constant of the reaction in which a complex substance is formed from simpler ones. Its reciprocal is the *dissociation constant* of the complex substance.

Exercises

1. Write an equation to represent the equilibrium between solid calcium carbonate (slightly soluble) and a saturated solution of that salt. What will happen, and why, when a small concentration of each of the following substances is added to the saturated solution just mentioned: calcium chloride, sodium carbonate, sodium sulfate, hydrochloric acid (which reacts with CO_3^{--} to form CO_2 gas)?

2. Suggest practical means for rendering silver sulfate less soluble than it is in pure water.

3. To reduce the solubility of lead chloride would you prefer to add a little calcium chloride to the solution or to add the corresponding concentration of ammonium chloride? Why?

4. In which of the following *very dilute* solutions will mercurous chloride be less soluble and in which more soluble than in pure water: solutions of KCl, $Hg_2(NO_3)_2$, $Ca(NO_3)_2$, $Al(NO_3)_3$? Explain.

5. Silver thiocyanate, AgCNS, at 25°C, is soluble to the extent of 2.1×10^{-4} gram-formula weight per liter. What is the activity product of this salt? $4.15\times$

6. Calcium fluoride at 25°C is soluble to the extent of 2.1×10^{-4} gram-formula weight per liter. What is the activity product of this salt? $9.3\times$

7. The activity product of lead sulfate, at 25°C, is 10^{-8}. What is its solubility, in gram-formula weights per liter? What is the normality of a saturated solution?

8. The concentration of a solution of a soluble oxalate is 0.05 gram ions of $C_2O_4^{--}$ per liter. What is the least concentration of Ca^{++} that will permit precipitation of calcium oxalate to begin? Explain why the concentration of Ca^{++} must gradually be increased as the precipitation proceeds. $4\times$

9. From the table in § 420 determine the activity product of silver bromide. What is the least concentration of Br^- that may precipitate Ag^+ from a $N/10$ solution of a soluble silver salt? 2.5×

10. Explain why several times the minimum concentrations found in the two preceding exercises must usually be taken, to cause visible precipitation.

11. By the interaction of solutions of ammonium sulfate and barium thiocyanate a precipitate of barium sulfate may be obtained. Describe the procedure to obtain this precipitate as a jelly or curd, as finely divided crystals, as coarse crystals.

12. Silver chloride can be obtained in crystals by dissolving the usual curdy precipitate in dilute ammonium hydroxide, then permitting the solution to evaporate slowly, just above room temperature. Explain why this procedure gives crystals.

13. Calcium sulfate is less soluble in hot water than in cold. Would you precipitate it in a hot or in a cold solution in order to obtain large crystals? Indicate other precautions.

14. What actual weight of silver nitrate would you dissolve in 100 ml to secure a concentration of 0.01 gram ion of Ag^+ in each liter? 170

15. Calculate the solubility of chromate ion, in gram ions per liter, in a solution of barium chromate containing 0.01 gram ion of Ba^{++} in each liter. 2×

16. What precaution would you take to insure that the precipitation of Ag^+ by SO_3^{--} might be as complete as possible? The precipitation of SO_3^{--} by Ag^+?

17. In the preceding exercise, which ion would turn out to be more effective in decreasing the solubility of the other? Why?

18. In the table in § 420 do large numbers correspond to large or small solubility? Refer to this table to determine the order of precipitation when a solution containing Ca^{++} and Sr^{++} reacts with a soluble carbonate.

19. What is the order of precipitation when a solution containing carbonate, oxalate, and sulfate ions is treated with Ca^{++} (refer to table, § 420)?

20. Find the least concentration of chromate ion that may cause the precipitation of silver ion from a tenth-normal solution of silver nitrate. 2×

21. Which of the following slightly soluble salts would you expect to be readily dissolved by acids, and why: $Ca_3(PO_4)_2$, $Ca(BO_2)_2$, AgBr, ZnS, $PbCl_2$?

22. Write an equation to represent an equilibrium between a precipitated heavy-metal hydroxide and a solution of its ions in water. The anion in this equilibrium is derived from what very slightly active acid? Explain why an active acid should dissolve such a precipitate.

23. Explain why most insoluble sulfides are dissolved by dilute solutions of active acids. Explain why a few sulfides fail to dissolve.

24. Write an ionic equation to represent the incomplete conversion of sulfate ion into acid sulfate ion, HSO_4^-, by reaction with an acid. What conclusion do you draw from this reaction concerning the effect of active acids on the solubility of slightly soluble sulfates, such as lead sulfate?

25. Cupric ion reacts with ammonium hydroxide to form tetrammine cupric ion. Express as a reversible ionic equation.

26. Write an ionic equation to express the precipitation of cupric hydroxide by adding an alkali to a soluble cupric salt. Then explain how the reaction of the preceding exercise may be used to redissolve the cupric hydroxide precipitate.

27. Explain whether the redissolving of a precipitate by the formation of a complex ion is favored or hindered if the reaction producing the complex ion is relatively complete. Also if a precipitate is extremely insoluble.

Chapter 31

THE COLLOIDAL STATE OF MATTER

428. Dispersions

The process of subdividing a material into smaller and smaller particles and scattering these through a second material is ***dispersion***. The result of the process is a ***dispersion*** or ***disperse system***. India ink is a dispersion of carbon particles in water; milk is essentially a dispersion of casein and butterfat in a solution of salts and milk sugar. The material that is subdivided and dispersed is often called the ***dispersed phase*** or ***inner phase;*** the other material is the ***dispersion medium*** or *outer phase.*

Dispersions are often classified according to whether the dispersed phase or the dispersion medium is a solid, liquid, or gas. Examples:

Chinaware or porcelain	an opaque *solid*, dispersed in a semi-transparent *solid*
Fogs, mist, or steam	a *liquid* (droplets of water) dispersed in a *gas* (air)
Biscuits or cake, pumice	a *gas* dispersed in a *solid*
Whipped cream	a *gas* (air) dispersed in a *liquid* (dispersions of this class are called *foams*)
Mayonnaise dressing, milk, or butter	a *liquid* dispersed in a *liquid* (dispersions of this class are called *emulsions*)
India ink	a *solid*, dispersed in a *liquid* (dispersions of this class are called *suspensions*)
Cheese	a *liquid* (butterfat) dispersed in a *semi-solid* (casein)
Smoke	a *solid*, dispersed in a *gas* (air)

Emulsions presently separate into two liquid layers, and foams collapse, unless stabilized by a small quantity of an ***emulsifier***. Soap serves as an emulsifier for air-in-water foams. Ordinary water-soluble sodium or potassium soaps will emulsify oil in water, whereas water-insoluble alkaline earth or heavy-metal soaps have the reverse effect and disperse water, in minute droplets, in oil as a dispersion medium.

The sizes of the dispersed particles in different sorts of dispersions have been measured in various ways. Diameters are usually expressed in millimicrons. One millimicron (1 mμ) is one millionth of a millimeter, namely 10^{-7} cm, or 10 Å.

Coarse Dispersions	*Fine Dispersions*	*Colloidal Dispersions*	*Solutions*
Dispersed particles visible to the naked eye	Dispersed particles visible under microscope	Dispersed particles below microscopic size	Dispersed particles are molecules or ions
Diameter, more than 50,000 mμ	Diameter, 100 to 50,000 mμ	Diameter, 1 to 100 mμ	Diameter, 0.2 to 1 mμ

The diameters here given are only approximate. Each of the four classes of dispersions has rather indefinite limits.

When the dispersed material has been subdivided to its very molecules (or ions) and these scattered through a dispersion medium, we have a *solution*. In a *colloidal dispersion*, often called a *sol*, the dispersed particles are of less than microscopic size, but are nevertheless enormous in comparison with molecules or ions. In a suspension of clay in water, or in an emulsion of kerosene oil in soapy water, the dispersed particles are still larger, and easily visible under the microscope or even with the naked eye.

With decreasing particle size the total *surface* of a given mass of material increases very rapidly. Colloidal particles owe their special properties, discussed in this chapter, to the fact that they possess relatively more surface than particles that are visible under the microscope or to the naked eye. The colloidal realm is the realm of exaggerated surface.

429. The Tyndall Test and Ultramicroscope

Colloidal dispersions are often as clear and transparent as true solutions, but may be recognized as colloidal by the famous *Tyndall test*, due to the British physicist John Tyndall (about 1881). If a beam of light is passed through a colloidal dispersion its path becomes beautifully illuminated (Fig. 134), since each of the colloidal particles reflects a portion of the light toward the observer. A true solution, under similar circum-

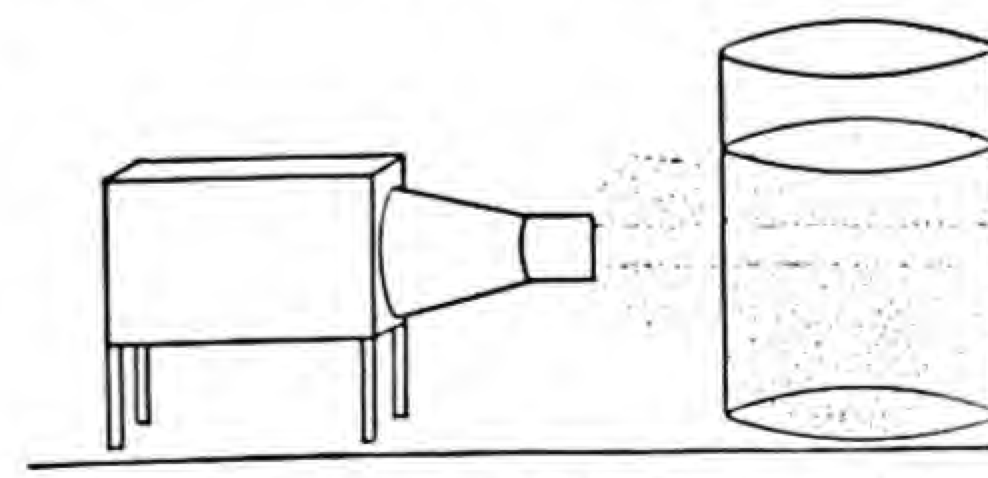


FIG. 134. The Tyndall test for colloidal particles.

stances, usually shows only a faint beam, owing to dust particles. A searchlight beam in a smoky or foggy atmosphere is another illustration of the Tyndall effect. So is a comet's tail.

When a colloidal dispersion is strongly illuminated and examined with a microscope, the colloidal particles become visible as a multitude of dancing points of light, particularly when the illuminating beam is rich in frequencies in the ultraviolet range—for as the invisible ultraviolet light is reflected sidewise by the individual colloidal particles

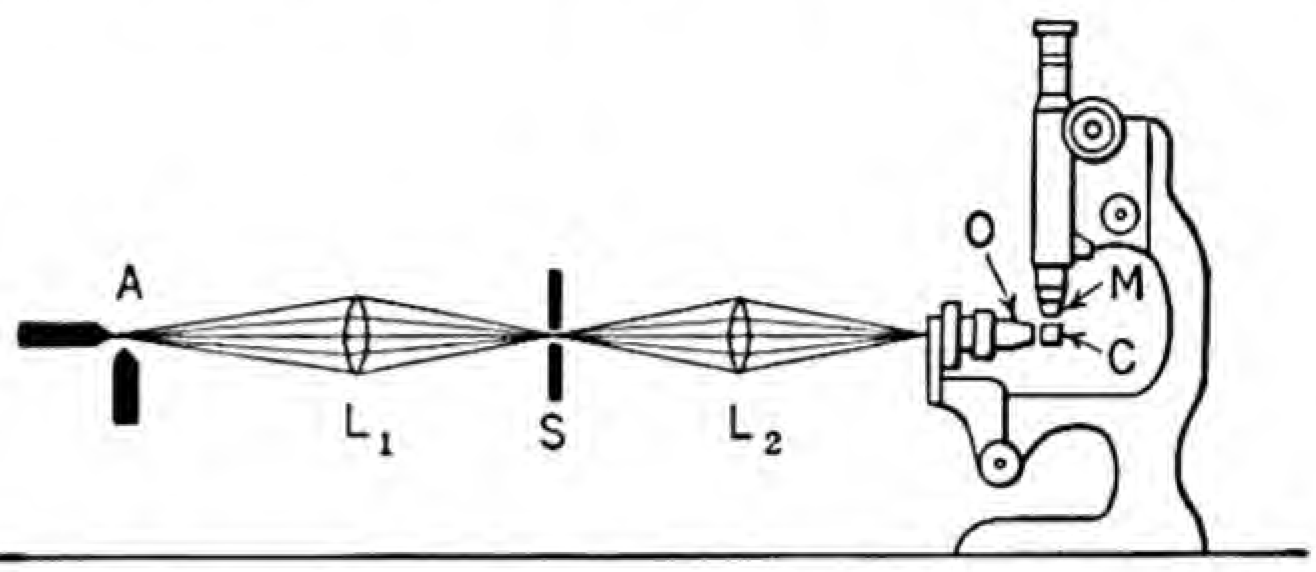


FIG. 135. Principle of the ultramicroscope. Light from an electric arc, at *A*, is passed through quartz condensing lenses, L_1 and L_2, and a slit *S*. The extremely intense needle-like beam thus obtained illuminates the colloidal particles within a small quartz-windowed cell, beneath the objective lens of an ordinary microscope.

its frequency is diminished, until it comes within the visible range of frequencies. This is the principle of the *ultramicroscope* (Fig. 135).

Using a colloidal dispersion of known concentration and actually counting the particles in a small known volume, with the ultramicroscope, one may easily calculate the *mass* and hence (from the density of the dispersed material) the *size* of an average colloidal particle. (Ex. 1.)

430. The Brownian Movement

Anyone who has used a compound microscope will have noticed that very small particles—specks of dust, pollen grains, or bacterial spores—are always in motion, swaying and jerking to and fro in a most erratic fashion. Whether they are of inorganic or organic origin seems to make no difference. The smaller they are the more violently they are agitated. With still smaller particles (colloidal particles) this *Brownian movement* is still more energetic. Anyone who has viewed their frenzied dance in the illuminated field of the ultramicroscope will never forget the sight. It is their vigorous movement, in random directions, that prevents colloidal particles from settling to the bottom of the containing vessel, as any very heavy visible or even microscopic particles (given time enough) are sure to do.

Since the Brownian movement of microscopic or submicroscopic particles is continued indefinitely and seems not to be influenced by the intensity of illumination, it seems reasonable to conclude that the particles are set in motion by collision with surrounding molecules of the dispersion medium. These, at any given temperature, have a definite average energy of motion (§ 73), which they impart to the Brownian particles in colliding with them. In other words, even particles large enough to be visible under the microscope possess the same energy of motion (averaged at any given moment) as ordinary molecules do at the same temperature. Particles that happen to acquire much more than this average energy move through long paths, thrusting the molecules of the medium aside. The rest move through short paths, and may appear merely to tremble or vibrate.

Since all sorts of Brownian particles possess the same average energy of motion, at any given temperature, they wander away (diffuse) from any given point toward any other at a rate that is determined by their *size* and by the *viscosity of the dispersion medium*, but is independent of their mass. The larger they are and more viscous the dispersion medium, or the lower the temperature, the more slowly they move.

Nevertheless, if molecules in general were less massive (that is, if it took more molecules to make a mole) the energy of an average molecule would be proportionately less. Brownian particles would then be less violently agitated by the impact of the molecules of the surrounding dispersion medium. So, by measuring (1) the rate of diffusion of Brownian particles or (2) the rate of migration of an individual particle in a specified direction, it is possible to calculate how many molecules compose a mole (details in textbooks of physical chemistry). The result turns out to be roughly 6×10^{23}, in agreement with other methods (§§ 182, 578) for deducing this constant, *Avogadro's number.*

431. Crystalloids and Colloids

When ionic substances or molecular substances of low molecular weight are dissolved, we commonly obtain a true solution. Such substances are often referred to as *crystalloids;* examples are the inorganic electrolytes (acids, bases, and salts) and such organic substances as glucose, cane sugar, and urea. Substances of complex composition or high molecular weight, on the other hand, are often referred to as *colloids* (*Greek:* like glue), for they commonly form colloidal dispersions when dispersed in another substance. Examples are cellulose, rubber, the vegetable gums, starch, and albumen (white of egg)—in brief, most

substances that consist of giant molecules formed by linking simple units into long chains, then frequently cross-linking chains to form networks.

The distinction between crystalloids and colloids is, nevertheless, very indefinite. In all probability, all substances may be made to assume either state. A colloid is not a substance of a particular chemical class, but rather one that tends to assume a particular physical state—a state in which it is subdivided to form particles of an extremely small size (1 to 100 mμ), which are dispersed or scattered through a second material. Common salt, for example, though it dissolves in water to form a true solution, may also be obtained as a colloidal dispersion when produced by precipitation in the midst of an organic liquid in which it happens to be insoluble. Conversely, such a "typical colloid" as rubber or egg albumen may be obtained in crystalline form, if proper precautions are taken.

432. Colloids and Life

To realize the overwhelming importance of colloids, one need but pause to consider that all the phenomena of life are connected with processes that take place only in colloidal matter. A seed is planted in the ground. Straightway there begins a contest for water, between seed and soil. In this contest, the seed wins, draws water into itself, and swells up until the seed-coat bursts. Here is a process that could never take place with crystalline material.

Presently growth begins. Little by little the stores of colloidal foodstuffs in the seed—starch, proteins, and fatty substances—are acted upon by enzymes, themselves of colloidal nature. Thus these reserves of food are converted into sugar and other crystalline material, transported in this form to growing stem or rootlet, and there rebuilt into colloid form. Soon the young shoot bursts from the soil, and unfolds its leaves in the sunlight. We then behold a new marvel—photosynthesis—the building up of starch, a complex colloidal material, from two simple crystalloids, water and carbon dioxide.

Thus the plant grows, perhaps at length becomes a tree, and after many years brings forth fruit after its kind. Roots, trunk, branches, leaves, bark, and fruit all consist of colloidal substances, with nowhere any other crystalloid than water, if we except a few simple substances, such as sugar and organic acids, which form no necessary part of the plant, but merely represent material in transport or storage, and destined in proper time to be itself elaborated into colloidal living tissue.

Nor are plants alone thus intimately related to the properties of colloids. Every individual animal is built up from complex material called *protoplasm*, which contains many different chemical substances, and assumes many different forms. But whether this protoplasm belongs to amoeba or to man, it is essentially colloidal. Large deposits of inorganic crystalloids are found in the animal body in only a few highly specialized structures, such as the bones and teeth (and are even there in intimate association with colloids). Mineral salts also play an important part in regulating the water-holding capacity of organized colloids.

433. Preparation of Colloidal Dispersions

Colloidal dispersions are frequently prepared by *dispersion methods*. These start with relatively large particles and break them down to colloidal dimensions. Occasionally, *simple grinding* will serve, in the presence of a suitable dispersion medium. More often, a *peptizing agent* or *protective colloid* is added—something that assists in the process of dispersion, doubtless by coating over the dispersed particles and preventing them from recombining to form larger particles. Thus a colloidal dispersion of graphite in water may be prepared by grinding in the presence of a little tannin; a colloidal dispersion of coal in petroleum by grinding in the presence of a little tar oil or rosin oil; and India ink by grinding lampblack in water in the presence of gum arabic.

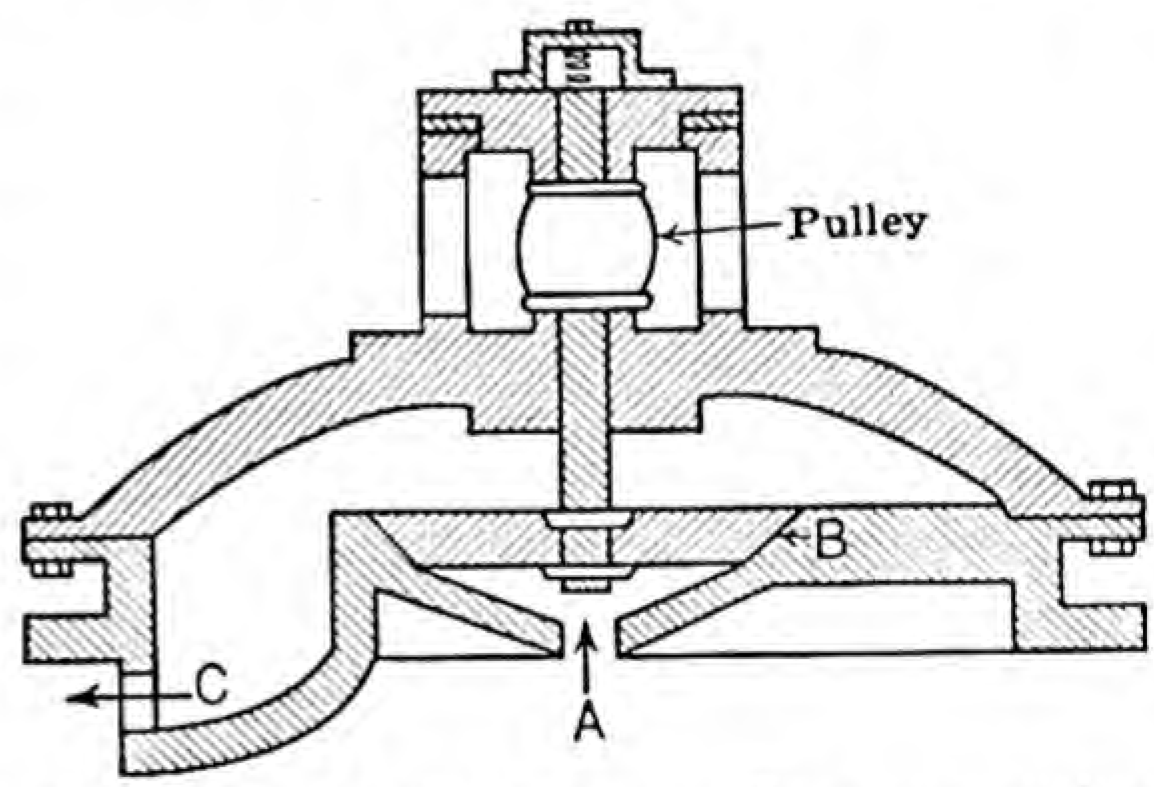


FIG. 136. Colloid mill. The suspension enters at *A*, is ground at the conical surfaces, *B*, and leaves at *C*.

Figure 136 shows a *colloid mill*, for preparing dispersions by grinding solid materials in the presence of peptizing agents. The dispersed particles are usually of distinctly more than colloidal dimensions, in spite of the name given to this equipment.

Certain materials are readily *peptized* (namely, dispersed to form a colloidal dispersion) *by mere presence of a dispersion medium*. Casein, precipitated by curdling milk with an acid, is readily redispersed to form a limpid colloidal dispersion by the addition of a little alkali; and pyroxylin (cellulose nitrate, § 467) is readily dispersed by a mixture of alcohol and ether, to form the viscous fluid known as *collodion*.

By contrast, other colloidal dispersions are prepared by *condensation methods*, in which molecules coalesce to build up particles of colloidal dimensions. For example, a solution of arsenic trioxide, As_2O_3 (a slightly soluble white solid), may be treated with hydrogen sulfide. Molecules of arsenic trisulfide, As_2S_3, so produced, coalesce to form colloidal particles. The resultant sol has not the least turbidity and readily passes through the pores of filter paper, yet betrays the presence of colloidal particles by the Tyndall test, and by the ready precipitation of these particles when a trace of an electrolyte is added (§ 436). Another example is observed when a solution of a gold salt is treated with a reducing agent, such as a trace of tannin. The reaction doubtless first produces individual atoms of metallic gold, which cling together when they collide, and so presently build up particles within the colloidal range.

Colloidal dispersions of gold, silver, and other metals in water or organic liquids are often prepared by striking an electric arc between electrodes of the metal, beneath the surface of the liquid. The metal is vaporized by the arc, the vapor then condensing to form particles that are mostly of colloidal dimensions. This is obviously a combination of dispersion, followed by condensation. Here again it is helpful to have some material present that may coat over the colloidal particles and prevent them from coalescing to form a precipitate.

434. Purification of Colloidal Dispersions by Dialysis

Some of the earliest experiments with colloids were performed by Thomas Graham, in 1861. It was he who first attempted to classify materials as crystalloids and colloids, and stated the law of diffusion of gases through porous walls (§ 111).

Graham found that colloidal particles are retained by porous membranes through which many crystalloidal particles pass readily. This may be illustrated by hanging a cellophane tube [1] containing water in a beaker containing a solution of common salt (a crystalloid) and starch (a colloid). After a few minutes some of the dissolved salt will have diffused through the walls of the tube and may be detected in the water within it by adding a few drops of silver nitrate solution and observing a white precipitate of silver chloride. If the cellophane membrane has no leaks no starch will get through it for many hours, as may be proved by adding a drop of iodine solution (which colors starch blue) to the water within the tube. Details are shown in Fig. 137.

[1] Use the grade of cellophane that is permeable to water, or remove the waterproofing from the impermeable sort by extraction with acetone.

Such a separation of two materials, by diffusion of one of them through a membrane, is called *dialysis*. It is commonly crystalloidal material that passes through the membrane, and colloidal material that fails to pass through. This is not so much due to the large *size* of colloidal particles in comparison to ordinary molecules as to their relatively great *mass*. In consequence, they move very slowly and hence are transferred very slowly by diffusion. Given time enough, a colloid that seems not to pass through ordinary membranes may really do so.

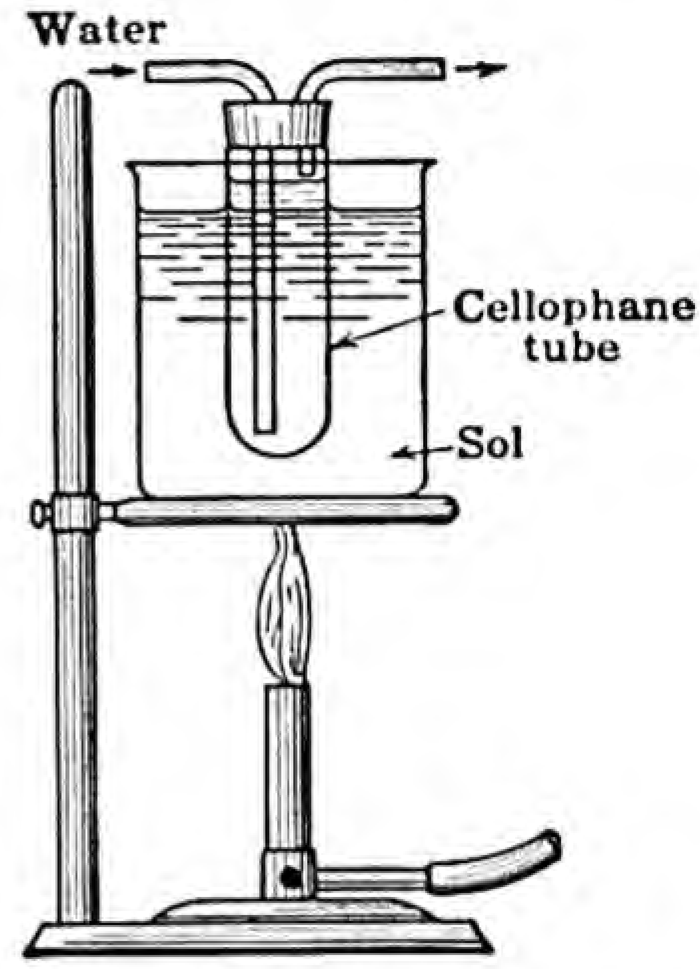


FIG. 137. Dialysis. It is best to place the sol to be dialyzed in the beaker and circulate water through the cellophane tube. The sol may then be heated, thus increasing the rate of dialysis, and evaporation from the surface of the beaker slowly concentrates the sol in spite of the passage of water outward by osmosis (§ 300).

435. Suspensoids vs. Emulsoids

Many colloidal dispersions, including most of those of *low viscosity*, are relatively *unstable*, and may be precipitated by slight traces of acids, bases, and salts (collectively known as *electrolytes*). Examples are aqueous dispersions of gold, graphite, clay, hydrous ferric oxide, and arsenic trisulfide. Materials that form such readily precipitable, non-viscous colloidal dispersions are called *suspensoids*, or *lyophobic colloids*.

In contrast with the dispersions just described are *viscous*, relatively *stable* dispersions, not readily precipitated by electrolytes. Many of them set to stiff jellies on being cooled or on altering the dispersion medium (§ 439). Examples are dispersions of gelatin, pectin, starch, or egg albumen in water; dispersions of rubber in benzene or other hydrocarbons; dispersions of pyroxylin (cellulose nitrate) in various solvents. Materials that form such viscous, jell-forming, relatively stable colloidal dispersions are called *emulsoids* or *lyophilic colloids*.

The essential difference between suspensoids and emulsoids is that emulsoid particles are penetrated by the dispersion medium, being thereby swollen and rendered semi-fluid. Surface tension then rounds them into spheres. Since the swollen dispersed particles are not so different in composition and density from the surrounding dispersion medium, the dispersion is relatively stable. Suspensoid particles, on the contrary, are not penetrated by the dispersion medium, hence remain dispersed only so long as they are electrically charged. (The

mutual repulsion between charges of the same sign tends to prevent the charged particles from colliding and coalescing to form particles that are heavy enough to settle out.)

436. The Charge Carried by Suspensoid Particles

The charge carried by a suspensoid particle seems to be due to ions that are adsorbed on its surface. Traces of impurities furnish a sufficient supply of ions to stabilize most suspensoid dispersions. In other instances the H_3O^+ and OH^- ions of water may serve. *Most suspensoid particles are negatively charged;* those of hydrous oxides of the heavy metals, hydrous ferric oxide for example, are positively charged.

Suspensoid particles are coagulated and precipitated by ions of opposite charge to themselves. Divalent ions are much more effective precipitants than univalent ions, and trivalent ions are more effective still. The SO_4^{--} ions in sulfuric acid are effective in precipitating the positively charged particles of hydrous ferric oxide sol; and the Ca^{++} or Al^{+++} ions [2] of a calcium or aluminum salt are effective in precipitating the negatively charged particles of an arsenic trisulfide sol.

If a small amount of arsenic trisulfide sol is added to hydrous ferric oxide sol, mutual precipitation takes place, and the two colloids are thrown down together. The negative charge of the arsenic trisulfide particles and the positive charge of the colloidal hydrous ferric oxide particles have neutralized each other. Suspensoids that precipitate each other almost always carry electrical charges of opposite sign. However, if a very large excess of either of the two colloids is used, the charge of the other one may be reversed, and precipitation may be prevented.

437. The Charge Carried by Emulsoid Particles

Emulsoid particles, instead of being definitely charged, either positively or negatively, are usually of indefinite and variable charge. Very frequently the charge on an emulsoid particle depends on a reaction in which the colloid acts as an *acid*, yielding protons, H^+, to the dispersion medium, thus being left negatively charged, or reacts as a *base*, accepting protons from the medium, thus becoming positively charged.

Emulsoid particles, of course, most readily yield protons, being left negatively charged, when they are surrounded by an alkaline solution;

[2] Probably complex ions, with aluminum salts.

and most readily gain protons, becoming positively charged, when they are surrounded by an acid solution. *For every emulsoid that may play this double role (i.e., for every amphiprotic emulsoid) there is a particular degree of acidity or alkalinity (for the surrounding medium) at which the emulsoid will act equally as an acid and as a base.* The emulsoid particles then lose their charge and are ordinarily precipitated. If they fail to precipitate they will at least show a minimum tendency to be penetrated by the dispersion agent, and the liquid in which they are dispersed will have minimum viscosity. The *p*H (§ 405) at which this happens is called the *isoelectric point* of the colloid.

438. Electrical Transfer of Colloids

The electrical charge on a suspensoid particle may be many times that carried by a univalent ion in a dilute electrolyte. The mass of each suspensoid particle is, however, very great, even when the particle is very small. The electrical conductivity of colloidal dispersions is therefore very low. A high voltage will nevertheless force a current through. With the apparatus of Fig. 138 the migration of the suspensoid particles, under the influence of the electrical potential, may easily be shown.

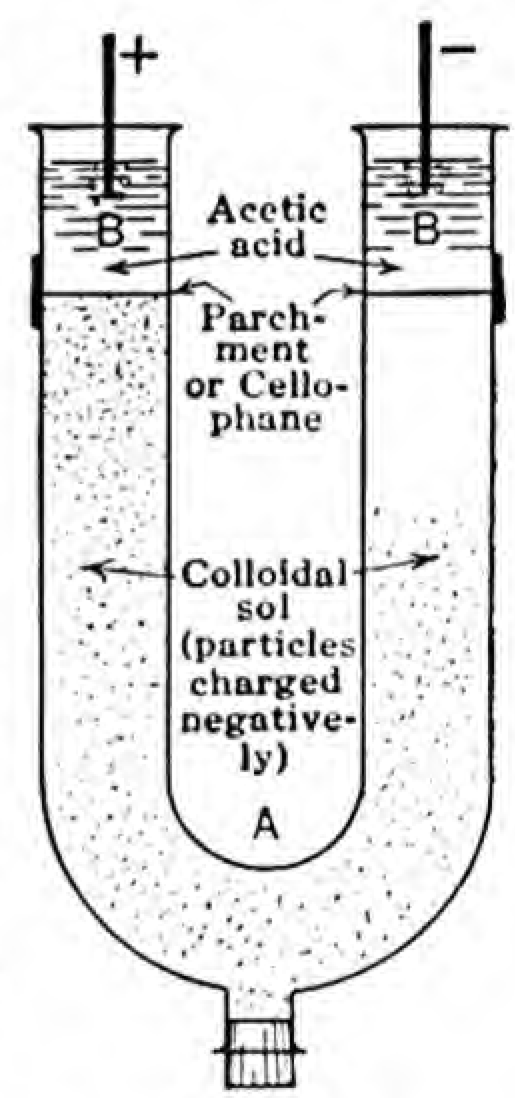


FIG. 138. Electrophoresis.

The ends of a U-tube (*A*) are covered with parchment paper. The tube is then inverted, filled through the opening at the bottom with colloidal arsenic trisulfide dispersion, and stoppered. Finally, two wide glass tubes (*B*, *B*), held in place by rubber bands, are slipped over the ends of the U-tube. After these have been filled with dilute acetic acid, and platinum or graphite electrodes inserted, the apparatus is connected with a 110-volt direct-current circuit. After half an hour the solution in the U-tube presents the appearance shown in the figure. Most of the suspensoid particles have migrated away from the neighborhood of the cathode (−), leaving that part of the liquid clear. The liquid around the anode (+) has in consequence acquired a deeper shade of yellow than before.

Such a transfer of colloidal particles in an electric field, each particle moving toward an electrode of opposite sign to itself, is sometimes called *electrophoresis*. The same principle is applied in the *Cottrell process* for precipitating dust from the fumes produced by cement kilns and smelters. The dust-laden gases are passed between two elec-

trodes, one of which is a wire with the same charge as the suspended particles, the other a plate with charge opposite to that of the particles. The particles are repelled by the wire, migrate to the plate, and are there discharged, coalescing to form particles large enough to settle.

If colloidal material is made into a porous plug, fixed in position between two charged electrodes, then any conducting liquid in contact with the plug will move through it in the opposite direction to that in which the colloidal particles themselves would have moved, if free to move. Thus moist clay (negatively charged) between two charged plates will separate liquid water at the surface of the negatively charged plate. Attempts have been made to decrease the tractive effort required to plow clay soils by charging the plowshare negatively, thus keeping it lubricated with a film of water.

439. Gels

Emulsoid dispersions frequently form semi-solid jellies, technically termed *gels*. These may be as much as 98 or 99 per cent water and only 1 or 2 per cent dispersed colloidal material (for example, gelatin or agar). A surprising number of the things met in ordinary life turn out to be gels. Examples are soaps, wood, rubber, a multitude of natural and artificial resins, and most of the tissues of our own bodies.

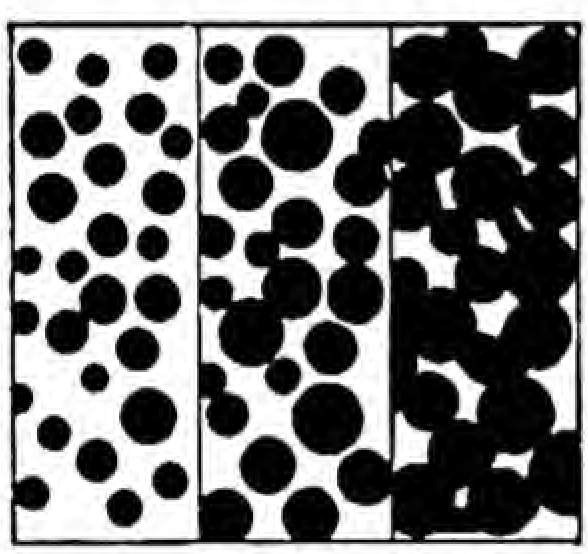


FIG. 139. Three stages in the formation of a gel.

Figure 139 illustrates what is believed to happen when an emulsoid sol sets to a jelly. At the left (A) we have a fluid sol, consisting of concentrated droplets of the disperse phase, scattered through a dilute solution constituting the dispersion medium. The effect of cooling such a sol is to disturb the equilibrium between the droplets and the surrounding dilute solution. We infer that they draw more water into themselves, and increase in size, and perhaps come into contact (as shown at B), like cells of a honeycomb. This change would result in a very great decrease of fluidity—for if one should attempt to stir such a mixture or force it through a tube the droplets would find much difficulty in rolling past one another. In the end the droplets may coalesce to form a network and we obtain a sponge-like structure (C)—a semi-solid gel. (Ex. 2–34.)

In addition to *aquogels*, in which the dispersion medium is water, we may encounter gels in which benzene or some other organic liquid is the dispersion medium. There are interesting *aerogels*, in which

silica, for example, though perhaps not visibly porous, may be so penetrated by air that a sample the size of one's fist weighs less than a gram! Gels are often formed by the cooling of a dilute solution (gelatin or fruit jelly, for example). Other gels are obtained directly by a chemical reaction (as in forming silica gel, § 483), or by replacing one solvent by another (as happens when we add chloroform to a dispersion of cellulose nitrate in amyl acetate).

Technical Words

Dispersion or **disperse system,** p. 494.

Dispersed phase or **inner phase,** p. 494.

Dispersion medium or **outer phase,** p. 494.

Foam—a dispersion in which the dispersed particles are gaseous.

Emulsion—a dispersion in which the dispersed particles are liquid.

Suspension—a dispersion in which the dispersed particles are solid.

Gel—a jelly or a gelatinous precipitate.

Aquogel, p. 504. **Aerogel,** p. 504.

Solution, p. 495. **Colloidal dispersion** or **sol,** p. 495.

Tyndall test—a test for colloidal particles, based on their ability to render the path of a beam of light luminous, by scattering a large proportion of the light that falls upon them.

Ultramicroscope—a microscope adapted for examining colloidal particles, under conditions that reveal them as minute points of light, in violent agitation.

Brownian movement—the erratic motion of microscopic or submicroscopic particles, caused by their collision with surrounding molecules of the dispersion medium.

Crystalloid—a material that is dispersed in most dispersion media to form a true solution rather than a sol.

Colloid—a material that tends to be dispersed to form a sol, rather than a true solution. Colloids usually have a complicated molecular structure and high molecular weight (details in § 431).

Peptizing agent or **protective colloid,** p. 499.

Emulsifier—A material (ordinarily a protective colloid) used to stabilize an emulsion by preventing or delaying the coalescence of the dispersed liquid particles.

Lyophilic—readily penetrated and swollen by a surrounding dispersion medium. When the dispersion medium is water the term **hydrophilic** is often used.

Lyophobic—not penetrated by a surrounding dispersion medium. If the dispersion medium is water the term **hydrophobic** is often used.

Isoelectric point—the *p*H at which an emulsoid colloid shows minimum swelling, often being nearly completely precipitated.

Electrolyte, p. 501. **Cottrell process,** p. 503.

Peptization—the dispersion of a material to form a sol, by the action of a dispersion medium.

Colloid mill—a mechanical device for reducing a material to particles approaching colloidal dimensions.

Dispersion or **disaggregation**—any process in which particles are reduced to smaller dimensions.

Condensation or **aggregation**—any process in which colloidal particles are built up from ordinary molecules.

Suspensoid, p. 501. **Emulsoid,** p. 501. **Electrophoresis,** p. 503.

Syneresis—slow, spontaneous shrinkage of a gel, accompanied by separation of liquid. Not all gels show this tendency.

Adsorption p. 382. **Dialysis,** p. 501.

Exercises

1. An observer counts 200 ultramicroscopic particles of colloidal gold. Treating these as spheres, each with a volume of $\frac{1}{6}\pi D^3$, in which D is their diameter, find their total mass, as a multiple of D^3. Gold has a density of 19.3 g/cm^3.

The gold particles just indicated were contained in a total volume of 10^{-9} ml. The concentration of the solution was 2.02×10^{-6} g/ml. Find the average diameter of the particles.

2. What is a dispersion? When is a dispersion classed as a true solution?
3. What is the unit commonly used in stating the size of very small particles? Express this unit in centimeters.
4. What is a sol? Why is the term "colloidal solution" an improper one?
5. Explain how the ultramicroscope is related to the Tyndall effect.
6. Why are the particles in the ultramicroscopic field always in motion? Why are they in more violent motion than the somewhat larger particles that are visible under an ordinary microscope?
7. Distinguish between crystalloids and colloids, with an example of each. Is this a sharp classification? Why or why not?
8. Distinguish between suspension and emulsion; between smoke and fog.
9. Pumice has sometimes been described as "solidified foam." Do you think this a good description? Why or why not?
10. What is an emulsifier? Give several examples of the use of emulsifiers.
11. What two general methods of opposite nature exist for preparing colloidal dispersions?
12. What are protective colloids? Do emulsifiers act as protective colloids?
13. Suggest a reason why the smoke from burning tar is usually very persistent and slow to settle.
14. By what test may suspensoids usually be distinguished from emulsoids?
15. Distinguish between the terms suspension and suspensoid; emulsion and emulsoid.
16. What are hydrophilic colloids? Mention an example.
17. What is a sol? How may one demonstrate that the particles in a suspensoid sol are electrically charged?
18. If the particles of two colloidal dispersions are oppositely charged they may precipitate each other on being mixed. Suggest an explanation.
19. What is meant by the Cottrell precipitation process? Mention some industrial applications.
20. What determines whether water emulsifies in oil or oil in water?
21. Explain what happens when a sugared fruit juice, concentrated and cooled, sets to a jelly.
22. Make a sketch to illustrate how dialysis is accomplished. Of what use is it?
23. What is adsorption? Mention some practical applications.

24. Tell how a colloidal dispersion of arsenic trisulfide is prepared. Explain why it cannot be prepared by passing hydrogen sulfide into a solution of arsenic trichloride, $AsCl_3$. (Note the other product of the reaction and the effect that it would have on the colloidal arsenic trisulfide.)

25. Distilled water must be used in preparing colloidal dispersions of metals in water; but in dispersing glue in water ordinary tap water may be used. Explain.

26. To what type of dispersion does each of the following belong: the smoke of a cigar; biscuits; fumes from boiling sulfuric acid; fumes of ammonium chloride, produced when a rod dipped in ammonium hydroxide is held over a solution of hydrochloric acid?

27. For what purpose does a housewife add pectin to fruit solutions being boiled down to form jelly? (Pectin is usually prepared commercially from apples or the inner rind of citrus fruits.)

28. Someone proposes to improve the atmosphere of a restaurant by circulating it over activated charcoal (§ 445). What benefit might this have?

29. An orchardist complains that his emulsion sprays are not very stable. Some one suggests the addition of a little skimmed milk. Does this seem reasonable? Why may this recipe be found to improve adhesion of the spray to the leaves?

30. What name is sometimes given to gels in which the dispersion medium is water? Those in which it is air?

31. Explain why it is an advantage first to emulsify an oil if one wishes to make it react with a reagent with which it will not mix.

32. A factory is greatly troubled by the tendency of an oily liquid to form stable emulsions with water. Filtering the emulsion through silica gel cures the trouble. Explain what probably happens.

33. Filter paper is a negatively charged colloid. Explain why a drop of arsenic trisulfide sol will spread uniformly through filter paper, whereas a drop of colloidal hydrous ferric oxide is immediately precipitated, only water spreading very far.

34. What is diffusion? Would you expect colloidal particles to diffuse more or less rapidly than ordinary molecules? Why?

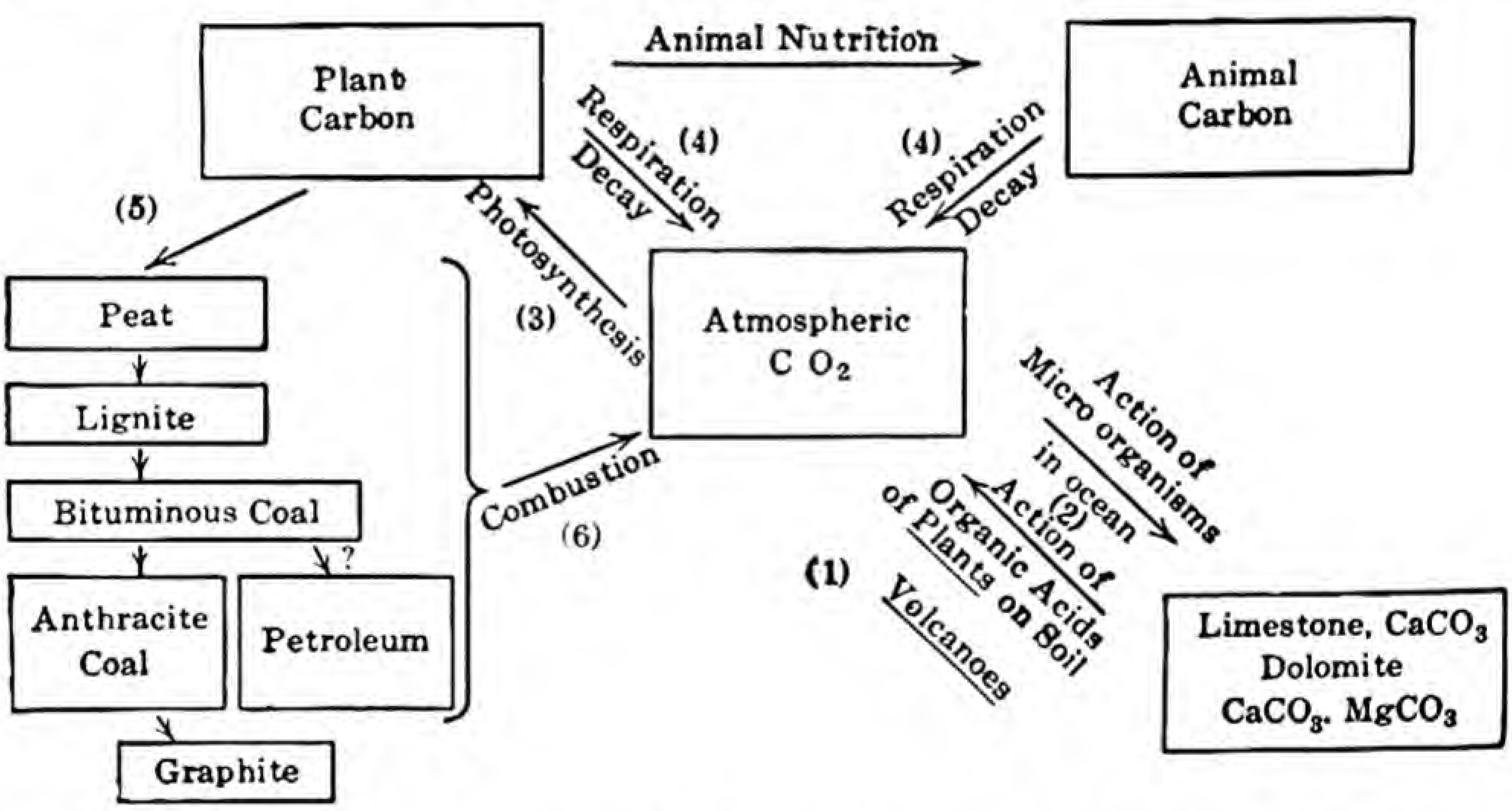
Chapter 32

CARBON

440. The Cycle of Carbon in Nature

Carbon makes up less than three hundredths of one per cent of the crust of the earth. Yet every continent contains inexhaustible supplies of carbon minerals, the *carbonates.* Limestone, chalk, and marble are examples. The atmosphere contains billions of tons of *carbon dioxide.* Vastly greater quantities still are dissolved in the ocean. *Coal* contains 60 to 80 per cent carbon, and *petroleum*, *wood*, and *peat* are mixtures of compounds of carbon. All living matter consists nearly altogether of carbon compounds, swollen with water.

Carbon, like nitrogen, passes through a definite cycle in nature:



1. By volcanic action, and by such human activities as in decomposing limestone to form quicklime (§ 531) and the production of iron in the blast furnace (§ 559), vast quantities of carbon dioxide are added to the atmosphere. The action of the organic acids of plants on the limestone of the soil releases further quantities. (Ex. 1.)

2. Carbon dioxide is withdrawn from the atmosphere by the activity of the organisms responsible for the formation of chalk and limestone beds, in the depths of the ocean.

3. Plants withdraw vast quantities of carbon dioxide from the atmosphere, and build it up into complex organic compounds of the most diverse sorts, at the expense of the energy of sunlight. This is photosynthesis (p. 516).

4. The respiration of plants and animals and their decay after life has ceased restore carbon dioxide to the atmosphere.

5. Plant material of former geological ages, compacted and chemically altered by pressure and heat, has produced *coal*.

6. By burning coal and other fuels we restore vast quantities of carbon dioxide to the atmosphere, from which it was long ago abstracted by photosynthesis. Thus the heat and light of burning coal represent energy stored up in the leaves of green plants, from sunlight that fell upon the earth more than a hundred million years ago.

The student should trace these six processes in the diagram on the preceding page.

441. The Structure and Properties of Diamond and Graphite

Carbon occurs in two crystalline forms, which differ strikingly in their properties. *Graphite* is black, flaky, soft, a good conductor of electricity. *Diamond* is colorless and transparent, the hardest of all known substances, and a non-conductor of electricity.

We find an explanation for this contrast of properties by a comparison of crystal structure, as determined by X-rays. The four valence electrons of each carbon atom enable it, by sharing electrons with four of its neighbors, to be linked with them in covalent union. In the diamond the four nearest neighbors of each carbon atom are symmetrically arranged about it in space (tetrahedral 4-coordination), in a cubic structure, as shown in Fig. 140. All the atoms in a diamond are thus firmly linked together, hence the whole crystal acts as a giant molecule. Thus we account for the extreme hardness of the diamond, its high melting point, and its failure to dissolve in any solvent.

If we could take a unit cube of the diamond and push one pair of diagonally opposite corners toward each other, all dimensions at right angles to the compressed axis would be lengthened. Each atom in every second plane of this flattened crystal could then drop into a space in the next lower plane. We would thus obtain *graphite*, which possesses *parallel planes of atoms*, each at a considerable distance from its neighbors, as in Fig. 141.

Each carbon atom in graphite has three nearest neighbors, all in its own plane. Only three of the four valence electrons of each atom are needed for furnishing bonds with these nearest neighbors, the fourth

being available for producing a bond with a neighboring plane. The planes are much farther apart than the atoms within each plane.

A certain proportion of the electrons in graphite are relatively free to move, as is true of metals (§ 492). In consequence, graphite is a

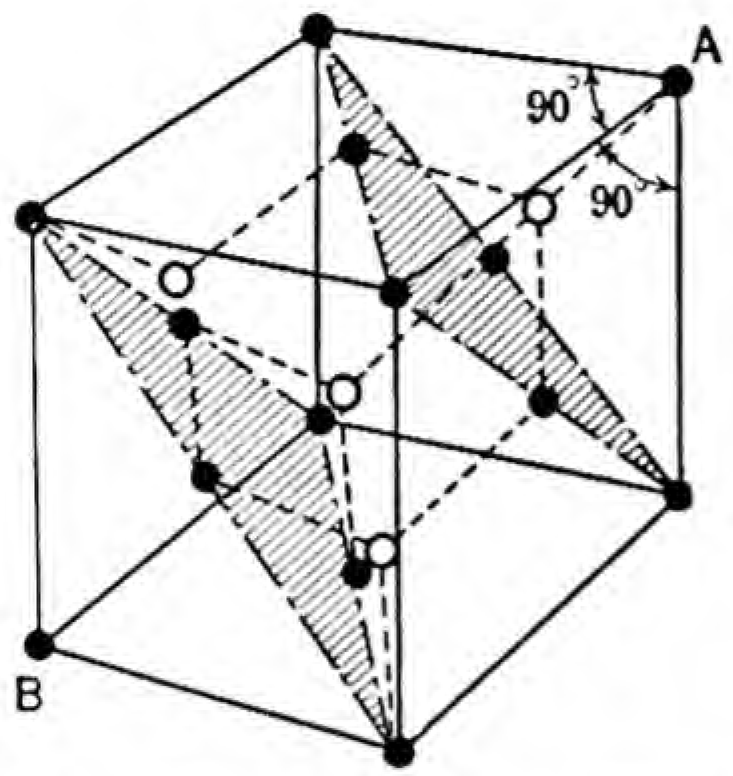


FIG. 140. The diamond lattice. It may be viewed as consisting of two separate face-centered cubic lattices, so interpenetrating that each atom of the one system is symmetrically surrounded by four atoms of the other.

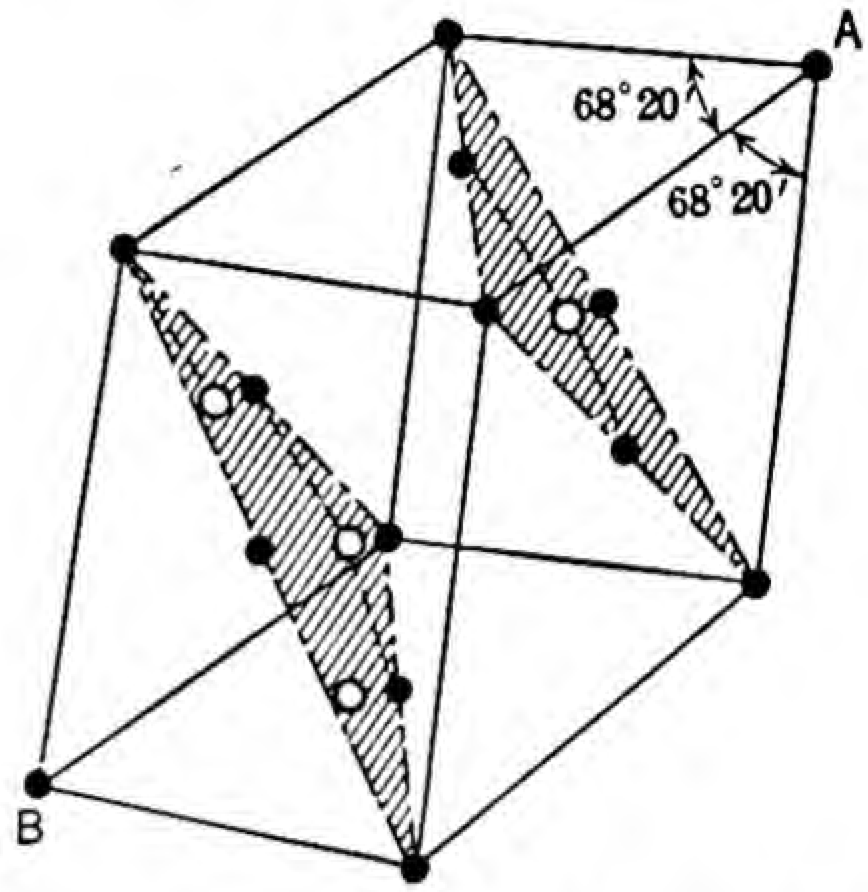


FIG. 141. The graphite lattice. Observe that it is produced by distortion of the diamond lattice so that two sets of atoms, which formerly occupied separate planes, are now all accommodated in the same plane.

conductor of electricity. When light falls upon graphite radiant energy is absorbed in setting the mobile electrons in motion. Graphite is therefore black and non-transparent, whereas diamond, with its electrons immobilized in strong bonds between the atoms, is colorless and transparent.

442. Graphite the Stable Form of Carbon

Graphite is the more stable form of carbon, though the transformation of diamond into graphite is imperceptibly slow at ordinary temperatures. If this were not so diamonds would soon lose their reputation for being a safe investment. At high temperatures the diamond is quickly converted into graphite. This change is, of course, accompanied by a decrease in potential energy (§ 67) in spite of an increase in volume. We see in this that, although the most stable crystalline form of any substance is usually that of minimum volume, this will not be so if formation of a different type of bonding enables transition to a larger volume to be accompanied by a decrease in potential energy, because of an extra close approach of the atoms in certain planes.

The close approach of the atoms within each layer of atoms in graphite insures that graphite, no less than diamond, is infusible, though it vaporizes at the temperature of the electric arc (3600°C). But the relatively great distance between the planes of graphite makes it soft—readily cleaving into flakes.

443. Preparation and Uses of Graphite

Graphite occurs in nature, but is chiefly produced by heating coke to high temperatures in an electric furnace. Ferric oxide in the ash of the coke serves as a catalyst, assisting in the formation of graphite crystals. The black color and flaky crystalline structure of graphite, its failure to oxidize readily, and its electrical conductivity are responsible for its chief uses:

1. As a heat-resistant material, in crucibles for melting metals.
2. In pencil leads (which are made of graphite, molded with varying proportions of clay, according to the hardness desired).
3. As an electrically conductive surface of powdered graphite, applied to a wax form, in *electrotyping*.
4. As electrodes, in arc lamps, and electric arc furnaces; or in granular form in resistor furnaces (§ 509).

444. Occurrence and Uses of Diamond

Diamonds occur in nature (South Africa and South America) in the weathered pipes of extinct volcanoes, and in neighboring places to which they have been transported by running water. The extreme hardness of diamond suggests its uses:

1. In drills and saws for cutting rocks.
2. In jewel bearings for watches, electric meters, and other instruments.
3. Diamond dust for polishing larger diamonds and other gems.
4. The filaments of incandescent light bulbs are made by drawing tungsten wire through conical holes bored through diamonds.

445. Apparently Amorphous Carbon

When organic material is heated in a retort, with only a sufficient opening to permit the escape of vapors, the material is gradually decomposed by the heat, various volatile products are given off, and impure carbon remains behind. The process is called *destructive distillation*. Wood yields *charcoal*, soft coal yields *coke*, and bones yield *boneblack*. *Petroleum coke* is formed by the destructive distillation of the non-volatile residue from the distillation of petroleum.

Coke usually contains 5 to 20 per cent ash. Metallurgical coke, used in reducing metals from their ores (§§ 507, 559), needs to be very dense and hard to resist crushing under the weight of the layers of ore and limestone charged above it in the furnace.

The materials just mentioned are not really amorphous (non-crystalline). Charcoal or coke is revealed by X-rays to consist of submicroscopic crystals of graphite, intermingled with tarry matter. On subjecting ordinary charcoal to the action of superheated steam, or even to a current of air under controlled conditions, the tarry matter may be removed and the crystalline structure accentuated. The result is *activated charcoal*, commonly used as an adsorbent for readily condensable gases in gas masks, or in condensing gasoline vapor from natural gas, in decolorizing sugar solutions, and in many other applications.

Lampblack is made by burning fats or oils in an insufficient supply of air, and *carbonblack* by burning natural gas in a limited supply of air. Lampblack is chiefly used for printer's ink, and carbonblack as a filler for rubber, to increase its toughness and wearing qualities. Every automobile tire contains several pounds of carbonblack. Even carbonblack and lampblack are not amorphous, but consist of submicroscopic flakes of graphite, one or more atoms thick.

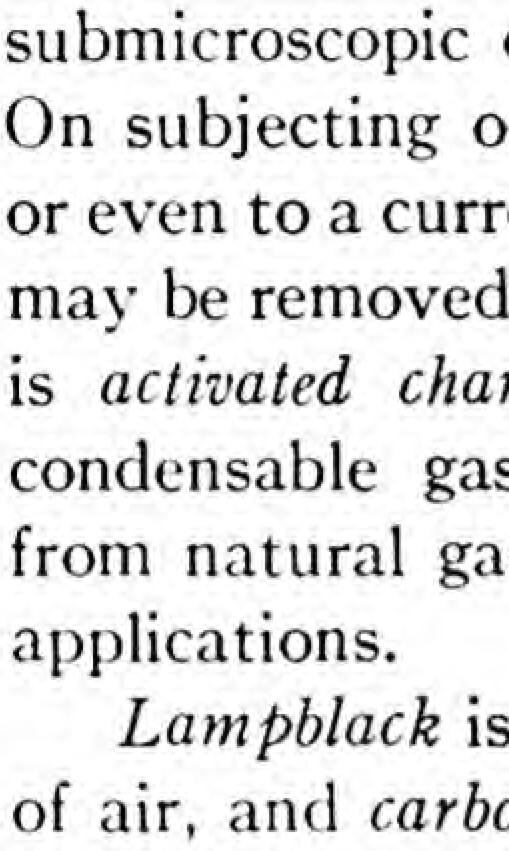


FIG. 142. Calcium carbide. The Ca^{++} and C_2^{--} ions occupy corners in two separate interpenetrating face-centered orthorhombic lattices.

446. Chemical Properties of Carbon

1. At high temperatures carbon combines directly with oxygen, with a few other non-metals, and with many metals.

2. When *silicon dioxide* is heated with carbon (coke) in an electric furnace it is reduced to elementary silicon, which then unites with an excess of carbon, forming silicon carbide, SiC. This has the internal structure of the diamond except that every other atom is replaced by silicon. In consequence, it is distinguished by extreme hardness and infusibility. (Ex. 2.)

3. Calcium oxide, heated in an electric furnace with an excess of carbon (coke), yields calcium carbide, CaC_2. This consists of calcium ions, Ca^{++}, of relatively small size, fitted between dicarbide ions, C_2^{--}, as shown in Fig. 142.

447. Carbon Dioxide

Carbon dioxide is produced on a commercial scale (1) by alcoholic fermentation of sugars; (2) from flue gases of steam boilers, or by burning carbon in an excess of air; (3) by calcining limestone (§ 531); and (4) from certain natural gas wells, which may supply nearly pure carbon dioxide. It is about one and a half times as heavy as air. It is fairly soluble in water, forming a solution that reacts slightly acid:

$$CO_2 + H_2O \rightleftharpoons \underset{\text{Carbonic acid}}{H_2CO_3}$$

Carbonic acid is classed as a *hypothetical acid*, since it has never itself been prepared, its existence being merely inferred from the formulas of salts and esters (§ 463) derived from it.

Carbon dioxide is quite stable at low temperatures, but at a white heat is partially decomposed into carbon monoxide and oxygen:

$$2CO_2 \rightleftharpoons 2CO + O_2$$

This equation is of importance in showing that a furnace may actually get too hot for complete combustion. The combustion of the fuel then yields a mixture of carbon dioxide and carbon monoxide, hence it liberates decidedly less heat than it would if it burned to form carbon dioxide alone.

Solid carbon dioxide (temperature, $-79°C$) is now widely used as a refrigerant in shipping fish and distributing ice cream. It passes directly from the solid to the gaseous condition, and surrounds the material to be refrigerated with an insulating atmosphere of dry gas. For this reason its refrigerating effect is about ten times that of an equal weight of a mixture of ice and salt, in spite of the fact that the calories absorbed per pound of solid carbon dioxide vaporized are less than twice the calories absorbed per pound of ice melted.

448. Carbon Monoxide

Carbon monoxide, CO, is produced in two ways:

1. By burning carbon in a limited supply of air.
2. By passing carbon dioxide through a layer of white-hot coke (as often in an ordinary stove or furnace, § 60):

$$CO_2 + C \rightarrow 2CO\uparrow$$

Carbon monoxide is intensely poisonous, since it combines with the red blood corpuscles, thus rendering the blood incapable of serving as a carrier of oxygen. Air containing as little as 1.5 parts of carbon monoxide in 1000 may prove fatal if breathed continuously. Since the gas is odorless it gives no warning until sudden paralysis may deprive its victim of ability to escape. Defective furnace flues or leaky rubber connections to gas stoves have often caused the death of entire households. A small automobile may generate a cubic foot of carbon monoxide a minute. This is sufficient to make the air of a closed garage dangerous to breathe within three minutes. Carbon monoxide is not adsorbed by charcoal; hence charcoal-filled gas-masks offer no protection against it.

Carbon monoxide is the usual *reducing agent* in reducing metals from their ores (§ 507). It is *an important component of many fuel gases*, such as water gas (§ 87) and *producer gas* (made by burning coal in a limited supply of air, to give a mixture containing about 60 per cent nitrogen, 30 per cent carbon monoxide, and 10 per cent hydrogen and hydrocarbons). Producer gas is often enriched by the addition of by-product gas from petroleum refining, since each cubic foot then releases more calories when burned. (Ex. 3.)

449. Carbon Disulfide and Carbon Tetrachloride

Carbon disulfide is produced by passing sulfur vapor over red-hot carbon, in a reaction chamber heated electrically or by burning oil. The carbon burns in the sulfur vapor, forming CS_2, just as it burns in oxygen to form CO_2. Carbon disulfide is a highly refractive, readily volatile liquid (boiling point 46.3°C). Its vapors are dangerously explosive when mixed with air, and so flammable that they may be ignited with a heated glass rod. (Ex. 4.)

Carbon disulfide is an important reagent in the manufacture of rayon and cellophane (§ 466), and is a solvent in the manufacture of matches and certain varnishes. It reacts with chlorine, in the presence of a little iodine, to serve as a catalyst, forming carbon tetrachloride and sulfur monochloride.

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2$$

The two products may be separated by fractional distillation. Carbon tetrachloride is used in fire extinguishers, in extracting oily seeds, and in dry cleaning. Sulfur monochloride is a vulcanizer for rubber. (Ex. 5.)

450. Calcium Carbide and Its Derivatives

Calcium carbide, CaC_2, is made by the action of an excess of carbon (coke) on quicklime in an electric furnace, at a temperature of about 2800°C:

$$CaO + 3C \rightarrow CaC_2 + CO\uparrow$$

Furnaces are so designed that the product melts and may be tapped off at the bottom of the furnace in a fused condition.

Calcium carbide reacts with water to form *acetylene:*

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2\uparrow$$

The chief industrial use of acetylene is in cutting and welding metals with the oxyacetylene torch. Acetylene is the starting point in a multitude of organic syntheses, including the production of alcohols, aldehydes, ketones, and esters, as described in the next two chapters.

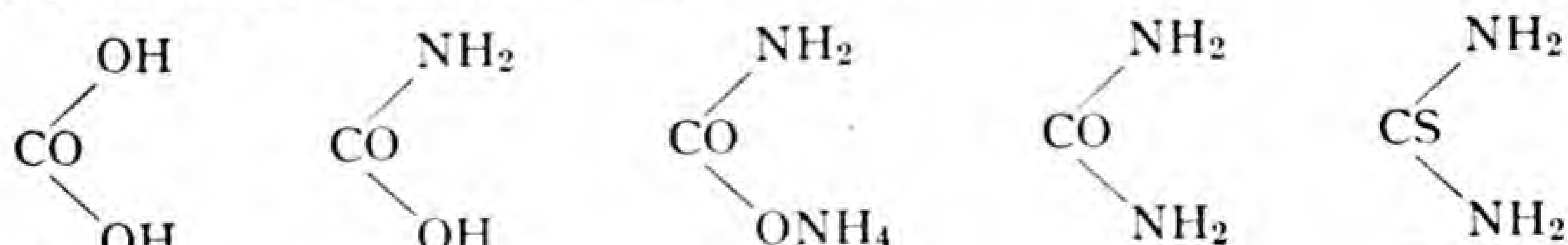
Calcium carbide combines directly with nitrogen at high temperatures to form *calcium cyanamide,* as already described (§ 367). This may then be converted into sodium cyanide by heating with carbon and a *flux* (p. 516), such as sodium carbonate or sodium chloride:

$$\underset{\text{Calcium cyanamide}}{CaNCN} + C \rightarrow Ca(CN)_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCN$$

This reaction is the chief source of cheap cyanide for the extraction of gold from gold ores. The success of this process has greatly increased the world's supply of gold, cheapened gold in relation to other commodities, and correspondingly increased the cost of living. (Ex. 6.)

451. Derivatives of Carbonic Acid

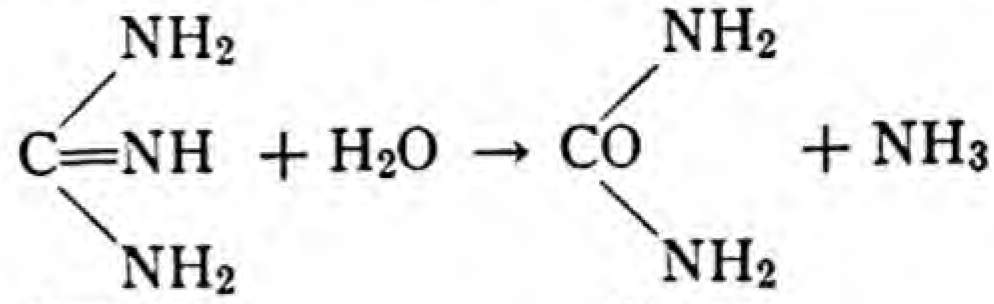
When carbonic acid reacts with ammonia the chief product is *ammonium carbamate.* When this is heated it loses water and is converted into *urea.* Compare the formulas:



Carbonic acid — Carbamic acid — Ammonium carbamate — Urea — Thiourea

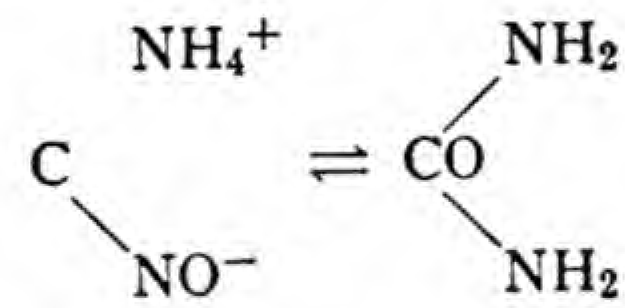
Urea can be prepared by heating ammonia, carbon dioxide, and water in a closed vessel, at about 120°C, but the yield is poor because the reaction gives several intermediate products and is reversible.

Commercially, urea is ordinarily prepared from cyanamide, H_2NCN. When this is heated with ammonia it yields *guanidine*, which is readily hydrolyzed in the presence of dilute acids, yielding urea:



Guanidine Urea

Urea is the form in which nitrogen is usually excreted by mammals. It was the first organic compound to be synthesized from inorganic materials (1828). The method was simply to evaporate a solution of ammonium cyanate:



Urea is of considerable industrial importance. It is sometimes used directly as a fertilizer, since it is gradually hydrolyzed in the soil with the production of carbon dioxide and ammonia. Plastics synthesized by the reaction of urea with formaldehyde are discussed in § 470. (Ex. 7.)

Technical Words

Photosynthesis—the synthesis by plants of organic compounds, with the aid of the energy of sunlight. The raw materials used are water and atmospheric carbon dioxide, and the active agent is chlorophyll, the green coloring matter of the higher plants and certain groups of algae. The solar energy used is chiefly that of frequencies in the red part of the visible spectrum. Since these frequencies are absorbed and the rest reflected, chlorophyll displays the complementary color to red, namely blue-green.

Calcining or **calcination**—decomposing or otherwise chemically altering a mineral or metal, by strongly heating it in the presence of air. (This is an alchemical term, now rarely used except in connection with the decomposition of carbonates by strong heating.)

Flux—a material which is added to another to obtain a mixture that melts at a lower temperature than either.

Destructive distillation—complete decomposition of a non-volatile organic material, by strong heating in the nearly complete absence of air.

Hypothetical acid, p. 513.

Exercises

1. What volume of carbon dioxide, recalculated to standard conditions, can be produced from 1 kg of limestone containing 12 per cent of siliceous impurities (SiO_2, etc.)?

2. Write an equation for the production of silicon carbide from silicon dioxide, assuming the other product to be carbon monoxide. How many moles of carbon monoxide are liberated for each kilogram of silicon carbide produced, if side-reactions are disregarded?

3. What volume of air, assumed to be 21 per cent oxygen, is needed for the complete combustion of 1000 cu ft of producer gas containing 60 per cent nitrogen, 30 per cent carbon monoxide, 5 per cent hydrogen, and 5 per cent methane, by volume? (The relative volumes of the gases concerned in the combustion are, of course, not altered by our use of cubic feet instead of liters.) 131

4. What products would you expect to obtain in burning carbon disulfide vapor in a plentiful supply of air?

5. In the reaction of chlorine with an excess of carbon disulfide vapor, how does the volume of chlorine and of the vapor of each product compare with the volume of carbon disulfide vapor transformed?

6. Write an equation for the action of nitrogen on calcium carbide, and explain how the mixture so obtained may be used to produce sodium cyanide, and to produce ammonia.

7. Write an equation for the hydrolysis of urea. What must usually then happen (§ 362) before the nitrogen can be used by growing plants?

Chapter 33

ORGANIC CHEMISTRY

452. Historical

A century ago the science of chemistry had already made a good beginning. All the most abundant elements and about half of the rarer ones had already been discovered. Methods of analysis had been developed by which individual metals and non-metals could be separated, identified, and determined quantitatively. The important minerals of the earth's crust had been analyzed and classified, and their formulas had been established. In the *inorganic* realm, chemical research pressed forward confidently, preparing new compounds of every known element, recognizing new principles, and creating new industries.

Meanwhile, at the threshold of the *organic* realm, the chemist paused in bewilderment. Living plants, with apparent ease, from water, carbon dioxide, and a few inorganic salts, created a multitude of compounds whose relationship to one another was completely hidden: celluloses, starches, sugars, fats, proteins, acids, alcohols, esters, and a few hydrocarbons! Then animals, from the complex organic materials created for them by plants, produced other marvels, including all the compounds demanded by the activities of organisms that move about, respond to a multitude of stimuli, and occasionally think.

The very name "organic," bestowed on the compounds of carbon by chemists of a century ago, implies that they believed that most of these compounds might never be produced except with the aid of "organized life," in other words, by living plants and animals. Only a very few carbon compounds, not very intimately related to life, had ever been made in the laboratory, and then only by accident, in default of all clues to manner of arrangement of the atoms in different sorts of organic molecules.

An important step toward a better understanding of organic compounds was made by the German chemist Liebig (1831) in the development of accurate methods for the determination of their percentage composition. Almost immediately, *organic radicals* were recognized—groups of atoms that remained unaltered in spite of transformations

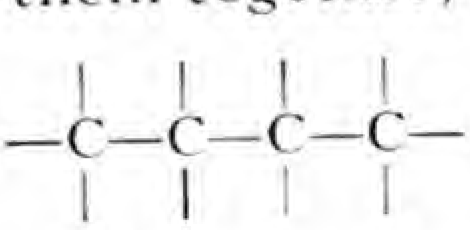
involving other parts of the molecule. Then Gerhardt, a pupil of Liebig (1842), was able to classify organic compounds into groups or series of closely related compounds, as they are recognized today. This was a most important advance, for it showed that the student of organic chemistry need not concern himself with a multitude of unrelated compounds, but might be content with becoming acquainted with a few outstanding classes or series of compounds—alcohols, aldehydes, ketones, amines, acids, esters, etc. Within each class the same general chemical behavior was to be expected, and an intimate study of a typical member of any class might lead one to anticipate what sorts of reactions would be entered into by all its other members.

Gerhardt next showed that simple inorganic formulas, such as HCl, H_2O, NH_3, suggest the formulas of important classes of organic compounds, in which *hydrocarbon radicals*, such as CH_3—(methyl) and C_2H_5—(ethyl), replace one or more hydrogen atoms of the inorganic compound. Then the English chemist Frankland (1852) developed the idea of *valence*, and the German chemist Kekulé (1858) observed that carbon, when it combines with other elements, nearly always has a valence of *four*.[1] He inferred that it must still have a valence of four even when it combines with itself to form organic radicals or molecules. Carbon, in a word, is *quadrivalent*. Here is the long-sought hidden key to the structure of the multitude of compounds that compose the universe of living things. (Ex. 1, 2.)

453. Chains and Rings of Carbon Atoms

When atoms of carbon combine with one another or with atoms of other elements, each becomes linked to its neighbors by four pairs of shared electrons, often represented by four strokes called valence bonds (§ 248). Let us consider four carbon atoms, each with four valence bonds:

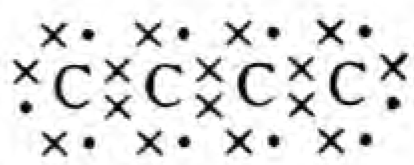
If these four carbon atoms become linked with one another, using some of the valence bonds to join them together, we obtain a chain of carbon atoms:



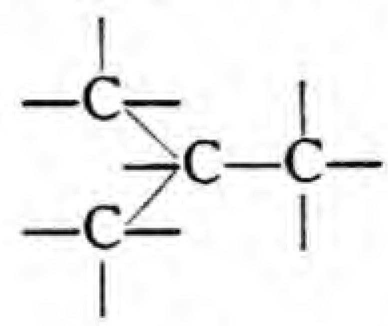
Each of the strokes (valence bonds) in these formulas represents a pair of electrons.

[1] We would now say, a *covalence* of four.

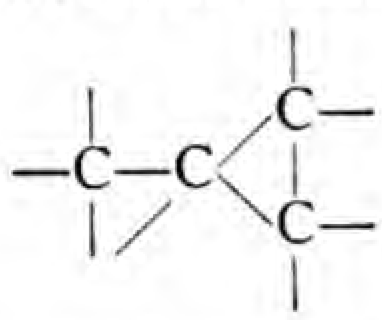
Using dots to represent electrons originally furnished by carbon, and crosses to represent those furnished by other atoms, such a chain of carbon atoms would appear:

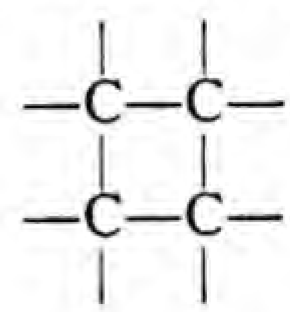


Such a chain might conceivably be *branched:*



Or three or four carbon atoms might be joined to form a *ring:*





Observe that four strokes (valence bonds) radiate from each carbon atom. Some of these are used in linking carbon to carbon. The rest are available for attaching atoms of any other elements we please. *This is important.*

At each end of a chain of linked carbon atoms an atom possesses *three* valence bonds, still unused. Within a chain or within a ring each atom may possess as many as *two* unused valence bonds; by using either or both of these to combine with additional carbon atoms we may obtain a branched chain, thus reducing the number of unused valence bonds on the original carbon atom to *one* or to *zero.*

The student should now take time out to see what can be done when we start with five carbon atoms instead of four. Link them together (single bonds) to form as many different types of chains and rings as can be made, giving each carbon atom four valence bonds. Then check against the following list of possibilities:

1. An unbranched chain of five atoms.
2. A chain of four atoms, with a fifth attached as a branch at either of the two non-terminal atoms. (To attach the fifth to a terminal atom would bring us back to the preceding case.)
3. A chain of three atoms, with two others separately attached at the middle atom of the chain.
4. A ring of five atoms.
5. A ring of four atoms, with a fifth attached as a branch, at any point.
6. A ring of three atoms, with a chain of two more, at one corner of the ring.
7. A ring of three atoms, with another attached at each of two corners.
8. A ring (square) of four atoms, sharing two atoms with a ring of three.

9, 10. Two rings of three atoms each, sharing two atoms in common, making four atoms in all. There are then two different ways of attaching a fifth atom.

Go over all these formulas to make sure that four valence bonds radiate from each carbon atom. (Ex. 3.)

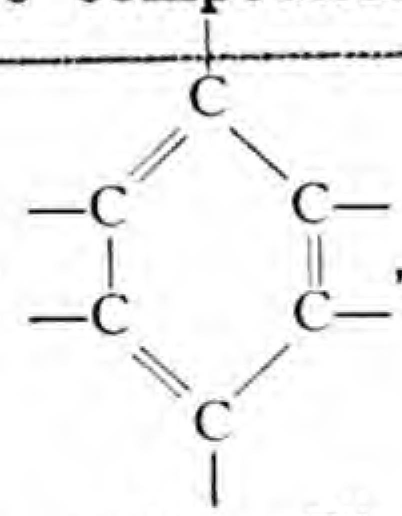
Every compound of carbon, no matter how complicated, may be considered as being composed of molecules formed by linking carbon to carbon, as just shown, to form an unbranched or branched chain, or a ring, or some combination of rings and chains. This constitutes the *carbon skeleton* of the organic molecule. If the unused valence bonds that then remain are used in attaching hydrogen atoms to the carbon skeleton we get a molecule of a *hydrocarbon*. If one or more of these bonds are used in attaching anything else than hydrogen or a hydrocarbon radical we get a molecule of some other kind of organic compound (§ 463). (Ex. 4.)

454. Four Great Divisions of Organic Compounds

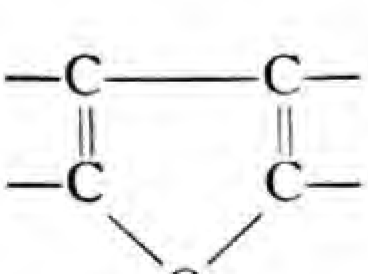
Organic compounds are classified into four great divisions, according to the carbon skeleton that the molecule happens to possess:

1. **Aliphatic compounds.** These have molecules composed of chains of carbon atoms, either branched or unbranched.

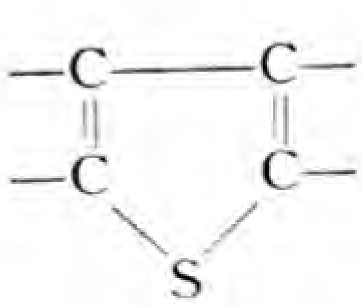
2. **Alicyclic compounds.** These have molecules containing one or more closed rings of carbon atoms, excluding the "benzene ring," next defined.

3. **Aromatic compounds.** These have molecules containing the benzene ring, , or a double or multiple ring derived from the benzene ring. The special manner in which the carbon atoms are bonded together in the benzene ring gives the aromatic compounds special properties (§ 461).

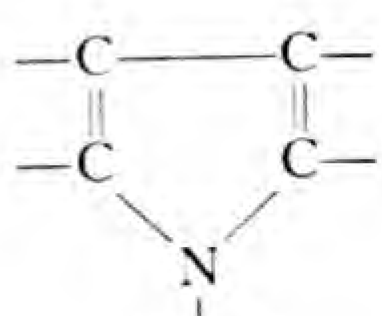
4. **Heterocyclic compounds.** These have molecules containing rings in which some of the atoms are of elements other than carbon or hydrogen. Examples of heterocyclic rings:



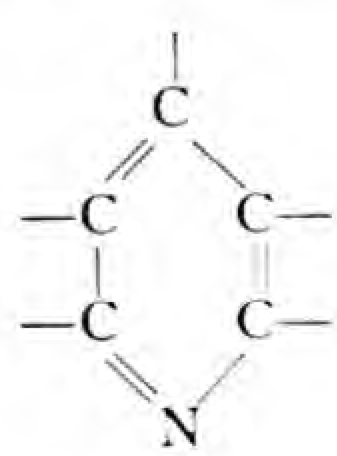
Furan ring



Thiophene ring



Pyrrole ring



Pyridine ring

455. Determining a Structural Formula

Organic compounds are, of course, never made in the laboratory by linking carbon atoms together to form a carbon skeleton, then attaching other atoms in sufficient number to satisfy unused valence bonds. Our exercise in linking atoms together is merely a basis for classifying compounds, not a method of synthesis. It is only on paper or on the blackboard that we can begin with elementary carbon, hydrogen, and a few other elements, and build up complex molecules as readily as preceding pages may have suggested. Yet formulas thus obtained usually correspond to compounds that are actually known or that we may hope to produce by appropriate reactions.

An outsider, listening to an organic chemist, is always very much impressed by the confidence with which the chemist lays out on paper a structural formula, representing the architectural plan of a molecule he proposes to build. He appears never to doubt that the atoms composing the molecule really are linked in unbranched or branched chains and rings, in the positions that he assigns them. He next proceeds to build the substance from molecules of a simpler sort, using his structural formula as a guide. At length, perhaps after a series of reactions taking weeks to carry through, he emerges with proof of his formula: a sample of synthetic camphor or rubber, or perhaps a dyestuff or local anesthetic, having properties often approximately predicted in advance!

Since the synthesis of an organic compound in the laboratory always needs to be guided by a structural formula, serving as an architectural plan of the molecule to be built, it is important to have a glimpse of the manner in which such formulas are deduced. As a simple example, let us see how the formula of ordinary alcohol (ethyl alcohol) was established. By burning a sample of alcohol, then collecting and weighing the carbon dioxide and water vapor produced, the *percentage of carbon, hydrogen, and oxygen* in the alcohol was determined. Its *molecular weight* was established by weighing a sample of the vapor, in comparison with the weight of the same volume of oxygen (§ 32). Knowing both the percentage composition and molecular weight we may derive the formula, C_2H_6O (§ 39).

We next turn to a study of some of the reactions in which ethyl alcohol is transformed. If we treat it with phosphorus trichloride, PCl_3, a hydrogen atom and an oxygen atom of the alcohol are *removed together*, and replaced by a chlorine atom. Thus we obtain ethyl chloride, C_2H_5Cl. This suggests that one hydrogen atom and one oxygen atom in the original alcohol are in such intimate union with

each other that if the oxygen atom is displaced from the molecule the hydrogen atom has to go with it. In other words, the alcohol molecule contains a *hydroxyl group*, $-OH$. Instead of C_2H_6O we may therefore write C_2H_5OH.

If we now give each carbon atom four valence bonds to connect with hydrogen or hydroxyl, we have the *graphic formula* (§ 248) of alcohol:

$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & OH \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

In practice we find that all the most essential information in this formula is retained if we condense it somewhat, to save space, and use a *condensed graphic formula* or *structural formula*, CH_3CH_2OH.

Two questions are commonly asked at this point by the chemical novice:

1. *Are these formulas for alcohol all equally correct?* Yes, so far as they go. Yet C_2H_6O fails to show that alcohol contains a hydroxyl group. It even leaves us in doubt which substance is meant. For methyl ether is likewise C_2H_6O, but with its atoms differently arranged, as given by the structural formula CH_3OCH_3.

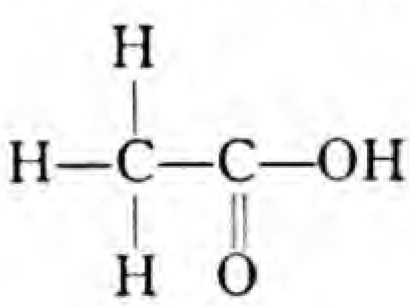
2. *When is the graphic or structural formula for alcohol preferred to the simple formula C_2H_5OH?* Whenever we need to show which particular hydrogen atoms are being replaced by atoms of other kinds, when alcohol is chemically altered.

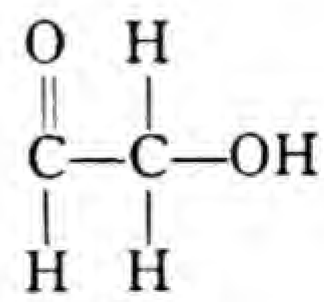
456. Another Example

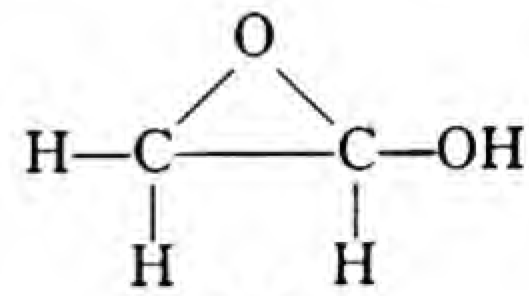
The percentage composition and molecular weight of acetic acid give us the formula $C_2H_4O_2$ (§ 39). When we treat the acid with phosphorus trichloride, PCl_3, we obtain a compound with the formula C_2H_3OCl. Comparing with the original formula, $C_2H_4O_2$, we see that one oxygen atom and one hydrogen atom of the acetic acid have taken their departure together and have been replaced by chlorine. We conclude that acetic acid, like alcohol, contains a hydroxyl group. Let us therefore write it $C_2H_3O(OH)$.

But carbon has a covalence of four, oxygen a covalence of two, and hydroxyl a covalence of one. Let us hook the atoms together in such a way as to give each carbon atom four strokes or valence bonds to connect it with other atoms, oxygen two valence bonds, and the hydroxyl group one valence bond.

If the reader will try this for himself he will discover that there are three possible ways of doing it. If the oxygen atom not in hydroxyl is attached by its two valence bonds to *the same carbon atom as the hydroxyl group*, the result is formula I, below. If it is attached to *the other* carbon atom, the result is II. If it is attached to *both* the carbon atoms at once, the result is III.


I


II


III

Which of these three possible formulas for acetic acid is the true one? To settle that question, note that *the three hydrogen atoms not in the hydroxyl group* are all attached to the same carbon atom, in I; but in II, and also in III, a part of them are attached to one carbon atom and a part of them to the other. Thus if a chlorine atom is substituted for a hydrogen atom, in formula I, to form monochloroacetic acid, the chlorine atom must always become attached to the carbon atom *not linked to hydroxyl.* But in II and III, the chlorine may replace hydrogen that is attached to the one carbon atom or to the other, and two products will be formed, which will be chemically different from each other.

Now all the efforts of synthetic chemists, down to the present hour, have produced but *one* compound derived from acetic acid by the substitution of a chlorine for a hydrogen atom. Thus of the three different possible formulas for acetic acid, there is no doubt that the first, more compactly written CH_3COOH, is correct. In brief, we note that chlorine, in replacing hydrogen in acetic acid, always replaces hydrogen that is attached to a given carbon atom; we conclude that there is no hydrogen on the other carbon atom. By analogy, if a passenger entering a subway train at a given station always becomes attached to a strap, we conclude that there are no seats. (Ex. 5, 6.)

With more complicated compounds than alcohol and acetic acid, attempts to determine the structural formula reduce to a process of *tearing down*, followed by one of *building up*. By tearing down a complex molecule, through the action of selected oxidizing agents or by hydrolysis (§ 396), we may arrive at substances of simpler structure, which may enable us to guess what the original structure might have been like. We are helped by knowing (1) that oxidation, once begun

at any place in a molecule, usually continues at that place until the carbon chain has there been broken; and (2) that oxidation of any chain attached to a benzene ring usually strips away the chain, leaving a *carboxyl radical,* $-COOH$, in its place.

After it has once been guessed what the structure of a complex substance may be, the *final test* is in seeing whether the substance may actually be synthesized, building the complex molecule, step by step, by appropriate reactions, with the presumed structural formula as a guide. With such complicated substances as camphor, quinine, indigo, the ingredients of natural perfumes, and the hormones (controllers of growth, vital activities, and personality, § 478) the verifying synthesis may take months or years of determined effort; but until it has been accomplished no one can be sure that the presumed structural formula is the true one.

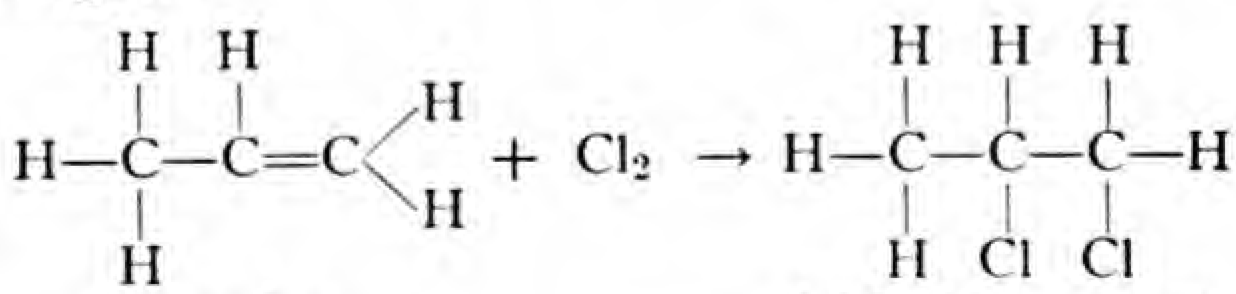
457. Saturated and Unsaturated Compounds

Many organic compounds *combine* with the halogens or with hydrogen (usually in the presence of a catalyst). Compounds of this sort are said to be *unsaturated.* Other organic compounds fail to react with the halogens except by *substitution,* one or more atoms of hydrogen (in each molecule of the compound) being *exchanged* for an equal number of atoms of halogen:

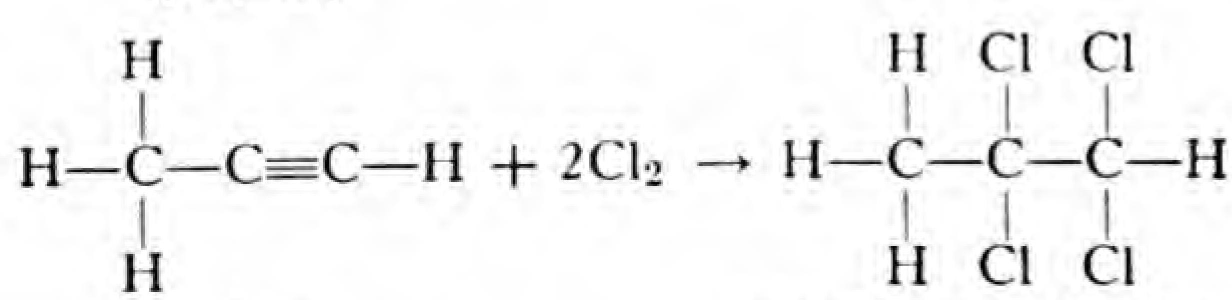
$$\underset{\text{Methane}}{CH_4} + Cl_2 \rightarrow CH_3Cl + HCl$$

Hydrocarbons which react with the halogens in this manner are said to be *saturated.*

The ability of the unsaturated compounds to combine with the halogens or hydrogen is due to their possessing double or triple bonds between neighboring carbon atoms. A double bond permits the direct addition of *two* atoms, and a triple bond the addition of *four* atoms, of halogen or hydrogen:



Propylene (propene) 1,2-Dichloropropane



Allylene (propyne) 1,1,2,2-Tetrachloropropane

Observe that the halogen atoms are added to the two carbon atoms that were originally linked by the double or triple bond, and that the latter is thereby converted into a single bond. The figures 1,2, attached to the name of the product, designate the carbon atoms with which the chlorine atoms are combined, numbering carbon atoms from the nearest end of a chain, or around a ring in any manner agreed upon. (Ex. 7.)

458. The Paraffin Hydrocarbons

If natural gas or the lower-boiling portion of American petroleum is subjected to elaborate and repeated fractional distillation, it can be separated (rather imperfectly) into a series of closely related *saturated* aliphatic (open-chain) hydrocarbons, of the general formula C_nH_{2n+2}, in which n is any number, from 1 to perhaps 30. These are the *paraffin hydrocarbons*. The first six members are:

Methane.	CH_4	Gas	B.P.	−164°
Ethane.	C_2H_6	Gas	B.P.	−85°
Propane.	C_3H_8	Gas	B.P.	−37°
Butane.	C_4H_{10}	Gas	B.P.	1°
Pentane.	C_5H_{12}	Liquid	B.P.	38°
Hexane.	C_6H_{14}	Liquid	B.P.	71°

Notice the fairly regular increase of boiling point with increasing molecular weight. The first four members are gases at room temperature, the next twelve are liquids, and the following ones are solids. Beginning with pentane, the names of the paraffin hydrocarbons are given by Greek numerals (Appendix G) that indicate the number of carbon atoms in the molecule.

The most conspicuous property of the paraffin hydrocarbons is their *chemical inertness*. They are not affected by prolonged boiling with concentrated sodium hydroxide or concentrated sulfuric acid; they react only very slightly or very slowly with such vigorous oxidizing agents as concentrated nitric acid or chromic acid. Chlorine and bromine, however, act upon them readily, a part or all of the hydrogen of the hydrocarbon being replaced by an equal number of atoms of the halogen. (Ex. 8.)

459. Isomers

There are actually two different butanes, three different pentanes, and five different hexanes, with the formulas assigned them in the preceding table, and a still greater number of each of the hydrocarbons of higher molecular weight. This multiplicity of compounds is due to the

fact that the carbon skeleton of the hydrocarbon molecule may be unbranched or branched.

The prefix *normal-* or *n-*, attached to the name of a compound, indicates an *unbranched chain*. Compounds with *branched chains* are often designated by the prefix *iso-*, but are better named by selecting the longest chain of carbon atoms in the molecule, numbering its carbon atoms, then indicating the numbers of the atoms to which branch chains (including the methyl group, CH_3—) are attached. The three pentanes are:

$$\underset{5}{CH_3}\cdot\underset{4}{CH_2}\cdot\underset{3}{CH_2}\cdot\underset{2}{CH_2}\cdot\underset{1}{CH_3}$$

n-Pentane

Boiling point (°C): 36.2

$$\begin{array}{cccc} & & CH_3 & \\ & & | & \\ \underset{4}{CH_3}\cdot & \underset{3}{CH_2}\cdot & \underset{2}{CH}\cdot & \underset{1}{CH_3} \end{array}$$

2-Methylbutane
(isopentane)

28

$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ \underset{3}{CH_3} & — & \underset{2}{C} & — & \underset{1}{CH_3} \\ & & | & & \\ & & CH_3 & & \end{array}$$

2,2-Dimethylpropane
(tetramethylmethane)

9.5

The three pentanes are said to be *isomeric compounds* or *isomers*—a name given to compounds having molecules that are identical except that the atoms within the molecule are differently arranged with respect to one another. Among hydrocarbons, isomers are due (1) to differences in the arrangement of the carbon atoms composing the carbon skeleton, or (2) to differences in the positioning of double or triple bonds. Among other classes of organic compounds isomers may arise from either of these two causes or (3) from differences in the positions occupied by atoms or groups that have been substituted for some of the hydrogen atoms of the hydrocarbons. Isomeric compounds are usually of very similar chemical properties, but usually are very different in melting point, boiling point, and often in solubility. (Ex. 9.)

460. Unsaturated Aliphatic Hydrocarbons

When the more volatile portions of petroleum are removed by distillation, a relatively non-volatile residue remains, consisting of paraffin hydrocarbons of higher molecular weight. By heating this residue to a high temperature, in the vapor or liquid state, in presence of a catalyst, the heavy molecules are broken down, with the production of the simpler molecules of more readily volatile hydrocarbons. This is the *cracking process* for the production of "cracked" gasoline, which accounts for about half the world's production of motor fuel. By contrast, "straight-run" gasoline is obtained by simply distilling off some of the more volatile hydrocarbons (heptane, octane, etc.), contained in petroleum, and "casing-head" gasoline by condensing or otherwise removing the more readily liquefiable hydrocarbons of natural gas.

A considerable part of the products of petroleum cracking consists of unsaturated aliphatic (open-chain) hydrocarbons often called *olefins* (*Greek:* oil-formers). Examples:

$CH_2{=}CH_2$	$CH_3CH{=}CH_2$	$CH_3CH_2CH{=}CH_2$
2 1	3 2 1	4 3 2 1
Ethylene (ethene)	Propylene (propene)	α-Butylene (1-butene)

$CH_3CH{=}CHCH_3$	$CH_2{=}CHCH{=}CH_2$
4 3 2 1	4 3 2 1
β-Butylene (2-butene)	Butadiene-1, 3 (a diolefin)

Observe that these unsaturated hydrocarbons have names derived from those of the corresponding paraffin hydrocarbons (§ 458), except that the ending *-ylene* or *-ene* replaces *-ane*. The position of the double bond is given by indicating the lower numbered of the two carbon atoms that it connects, as in butylene-2. (Ex. 10–12.)

The olefins, on account of their chemical reactivity, are important raw materials in the production of many different industrial products. They combine directly with hydrogen, forming *saturated hydrocarbons;* with chlorine or bromine, forming *halogenated* hydrocarbons; sometimes (in the presence of catalysts) with ammonia, forming *amines* (§§ 463, 464) and with water, forming *alcohols*. Thus propylene combines with water to form *isopropyl alcohol*, which in turn may be oxidized to form *acetone:*

$$\underset{\text{Propylene}}{CH_3CH{=}CH_2} + HOH \rightarrow \underset{\text{Isopropyl alcohol}}{CH_3CHOHCH_3} \xrightarrow[\textit{Oxidation}]{} \underset{\text{Acetone}}{CH_3COCH_3}$$

Isopropyl alcohol and acetone are both important solvents in the lacquer industry. Ethylene, in several steps, may be converted into *glycol*, CH_2OHCH_2OH, familiar as an anti-freeze under the trade-name *Prestone*.

More important yet, *olefin molecules combine with one another*. The double bond (in the presence of a catalyst) acts as if it furnished a pair of unused valence bonds:

$$\underset{\text{Propylene}}{CH_3 \cdot CH{=}CH_2} \rightarrow \underset{\text{Activated form of propylene}}{CH_3\overset{|}{C}H\overset{|}{C}H_2}$$

Two such activated molecules may combine, often in several different ways, thus doubling the length of the carbon chain. In this way, propylene gives several different isomeric hexylenes, such as:

$$\underset{\substack{\alpha\text{-Hexylene} \\ \text{(1-hexene)}}}{CH_3CH_2CH_2CH_2CH{=}CH_2}$$

A third and fourth molecule may then combine with the hexylene, to form a long chain of carbon atoms, and ultimately perhaps a tarry or resinous product.

Any reaction in which identical molecules combine, *creating new carbon-to-carbon linkages*, is termed *polymerization*. The product of such a reaction is called a *polymer* of the original substance. Distinguish polymerization from *association* (§ 123), in which identical molecules become reversibly and less firmly linked, *ordinarily through a hydrogen bond* (§ 272). (Ex. 13.)

Kekule's dream

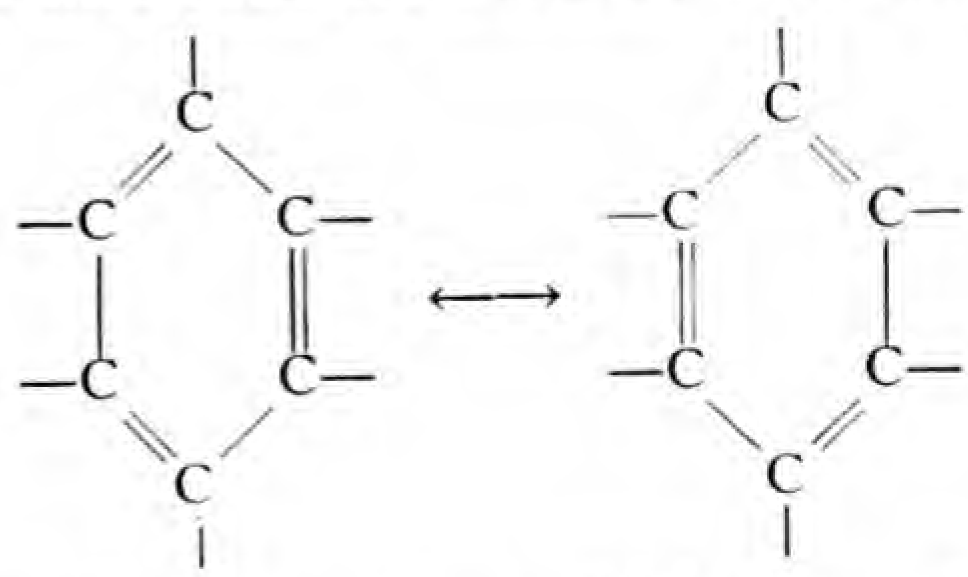
461. Aromatic Hydrocarbons

ring structure compounds

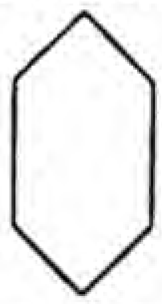
Benzene, C_6H_6, the simplest of the aromatic hydrocarbons, lacks eight atoms of hydrogen, in comparison with hexane, C_6H_{14}, a paraffin hydrocarbon. Such a deficiency in hydrogen would ordinarily result in ability to combine with hydrogen or with the halogens, by direct addition. In other words, we might reasonably expect that a hydrocarbon so deficient in hydrogen as benzene would behave as if unsaturated. Actually, it does not. Benzene can be made to combine directly with the halogens, but with difficulty, and it shows no trace of the tendency to polymerize, which we have just seen to be an important characteristic of compounds that are truly unsaturated.

Kekulé, in 1865, assumed that the molecule of benzene has a ring of six carbon atoms. The ring obviously gains increased stability and is rendered less reactive by some type of carbon-to-carbon linkage that is quite different from anything known among aliphatic or alicyclic compounds.

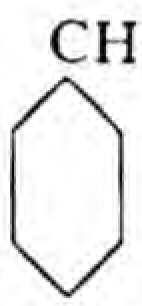
The special manner in which the carbon atoms are linked in the benzene ring gives the aromatic compounds special properties. Perhaps the simplest expression of modern views is to say that the benzene ring has a structure intermediate between two formulas:



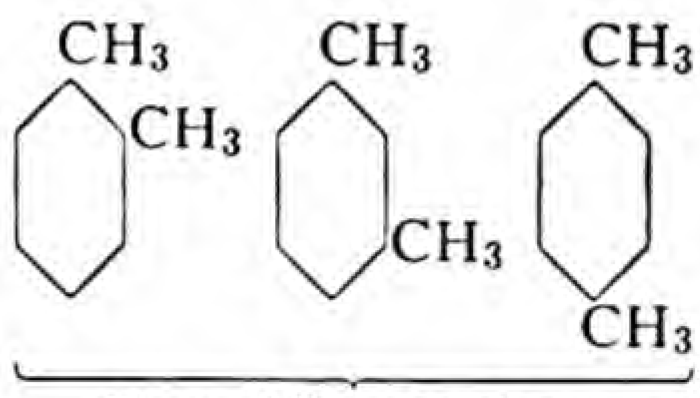
Observe that a pair of carbon atoms which in one formula is connected by a single bond (a single pair of electrons) is in the other formula connected by a double bond (two pairs of electrons). The double-

ended arrow is used as a symbol of *resonance*—a state intermediate between those represented by two closely related formulas, and more stable than either. This is much as if pairs of carbon atoms, around the benzene ring, instead of being linked alternately by single and double bonds, were all linked by "$1\frac{1}{2}$–bonds" (3 electrons each). In complicated formulas (examples hereafter) the benzene ring is usually represented by , leaving unexpressed the 6 carbon atoms and any hydrogen atoms that may be attached to them.

Benzene is the most volatile of the components of *coal tar*, an evil-smelling black liquid obtained by the destructive distillation of coal. It is there present with various substituted benzenes, in which hydrocarbon groups *replace hydrogen atoms* at one or more corners of the benzene ring:



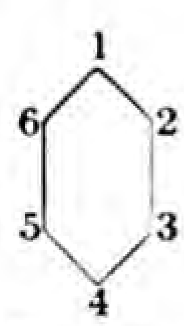
Toluene



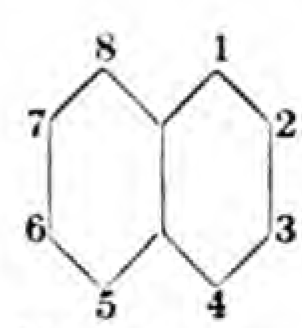
Three different xylenes

At each of the *unoccupied* corners of these hexagons there is CH, as in benzene itself. At each *occupied* **corner** H has been replaced by CH_3, giving $C—CH_3$, which is represented by CH_3.

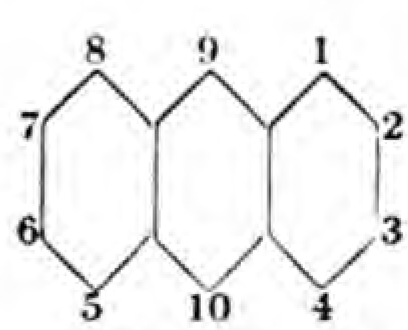
In addition, coal tar yields a number of compounds with multiple or *condensed* benzene rings:



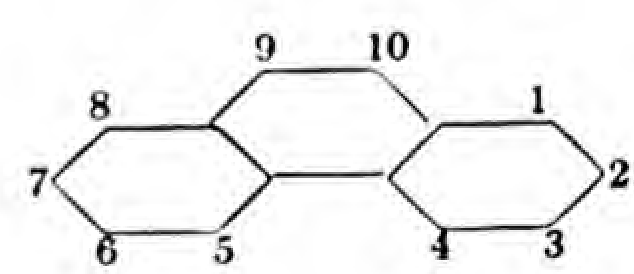
Benzene



Naphthalene



Anthracene



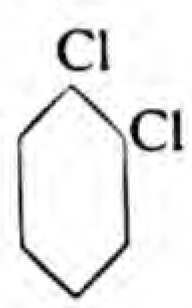
Phenanthrene

We have here indicated the numbers used to distinguish different CH groups around the rings, whenever one or more hydrogen atoms in these groups are replaced by other atoms or groups. The six positions around the benzene ring are really identical, also the 1,4,5,8 positions, 2,3,6,7 positions, and 9,10 positions, around the naphthalene and anthracene rings, since any one of these positions may be brought into any other by turning the molecule upside down or end for end. Unnumbered corners represent C, rather than CH, hence need not be numbered, for no other atom or group can ever become attached at these points by replacement of hydrogen, but only by altering the ring structure completely. (Ex. 14.)

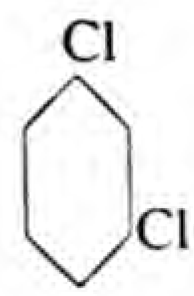
A ton of bituminous coal will usually yield about 10,000 cubic feet of coal gas (chiefly hydrogen and methane), with 1300 pounds of coke, 5 pounds of ammonia, and about 12 gallons of coal tar. The coal tar will yield about 10–14 pounds of benzene, 3–4 pounds of toluene, and smaller quantities of other aromatic hydrocarbons.

462. Positioning Substituents Around the Benzene Ring

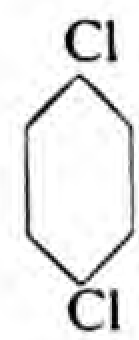
When other atoms or groups of atoms are substituted for hydrogen, around the benzene ring, we need to know where they go. If there are two substituting atoms, for example, do these go into adjacent positions (I), or are they spaced a third of the way around (II) or halfway around (III)?



I
Adjacent
Ortho (or 1,2)-dichlorobenzene



II
2 Steps Removed
Meta (or 1,3)-dichlorobenzene



III
Opposite
Para (or 1,4)-dichlorobenzene

It is easy to see that there should be three different isomers for all twice-substituted benzene derivatives, according as the substituting groups are adjacent, two steps removed, or opposite. Actually, *whether the two substituting atoms or groups are alike or different, three different isomers are always known.*

The problem, then, is to discover whether the two substituting atoms or groups in any given twice-substituted benzene derivative are separated by a step, skip, or jump. Kekulé recognized this problem but failed to solve it. It demanded ten more years of incessant labor on the part of many investigators. Then the clue was furnished by Körner, a pupil of Kekulé. It was simply *to note how many thrice-substituted compounds can be prepared from a given twice-substituted compound.* (Ex. 15.)

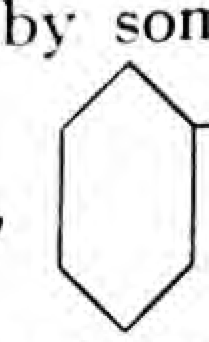
The architectural plans of twice-substituted molecules having been disclosed, it was easy to pass from these to thrice-substituted molecules, and so on. With a few more years of effort, the spacing of the substituting atoms and groups around the benzene ring was worked out for a great multitude of aromatic compounds. By 1885—twenty years from the time of the first paper of Kekulé on the benzene ring—the problem of relative position was practically solved. Today you may buy many benzene derivatives in carload lots, with the substituting groups placed anywhere you specify. If you would have them in

adjacent positions, ask for an *ortho* (or 1,2) compound; in positions two steps removed, a *meta* (or 1,3) compound; in opposite positions, a *para* (or 1,4) compound. Usually these prefixes are represented by their initial letters: *o*, *m*, *p* (as in *o*-cresol, *m*-cresol, *p*-cresol). The compounds thus distinguished, though of very similar chemical properties, are often physically quite different. One of them may be a solid, and the other two liquids of different boiling points. If you build them into a dyestuff or perfume, the color or odor that you get will generally vary from one isomer to another. (Ex. 16.)

463. Compounds Classified by Reactive Groups

In what precedes we have implied that every organic compound may be viewed as if derived from some hydrocarbon by replacing one or more hydrogen atoms of the hydrocarbon by other atoms or groups of atoms. For that reason *organic chemistry* is often defined as the chemistry of the hydrocarbons and their derivatives.

The parent hydrocarbon contributes to each compound a definite carbon skeleton: a simple unbranched chain of carbon atoms, or a branched chain, or one or more rings, with or without side-chains at particular corners of any ring. This carbon skeleton does much to determine the physical properties of the compound, and to a limited extent may influence its chemical properties, particularly when we pass from an aliphatic or alicyclic compound to an aromatic one. Chemical properties are nevertheless chiefly determined: (1) by certain *reactive* or *functional atoms* or *groups*, which have replaced one or more hydrogen atoms of the parent hydrocarbon; (2) by double or triple bonds. There are numerous classes of organic compounds, each characterized by a particular reactive group, as shown in table on p. 533.

For the *methyl group*, CH_3—, in the last two columns of our list, we may substitute (on paper) an *ethyl group*, C_2H_5—, or some other aliphatic hydrocarbon group, to obtain a different *aliphatic* member of the same class of compounds. Thus methyl alcohol, CH_3OH, becomes ethyl alcohol, C_2H_5OH. If the methyl group is replaced by some aromatic hydrocarbon group, such as the phenyl group,  or C_6H_5—, the result is an *aromatic* compound, *e.g.*, C_6H_5OH, phenol. In every important class of organic compounds there are thousands of individual compounds—as many as there are different practically possible points of attachment of the characteristic reactive atom or group, when attached to all possible carbon skeletons!

Nevertheless, for all the compounds of any one class—for all the aldehydes, let us say—there are a definite set of reactions, easily learned, that characterize the class. That would seem to make organic chemistry simple and easy. Unfortunately, variations in the carbon skeleton do cause certain departures from the normal behavior of the members of any given class of compounds. Worse yet, a compound may belong to two or more classes at once, being both an aldehyde and a nitrile, for example, because one of the atoms of its carbon skeleton carries a —CHO group and another a —CN group. So the writing of organic structural formulas and their use in predicting reactions is really a bit complicated, after all.

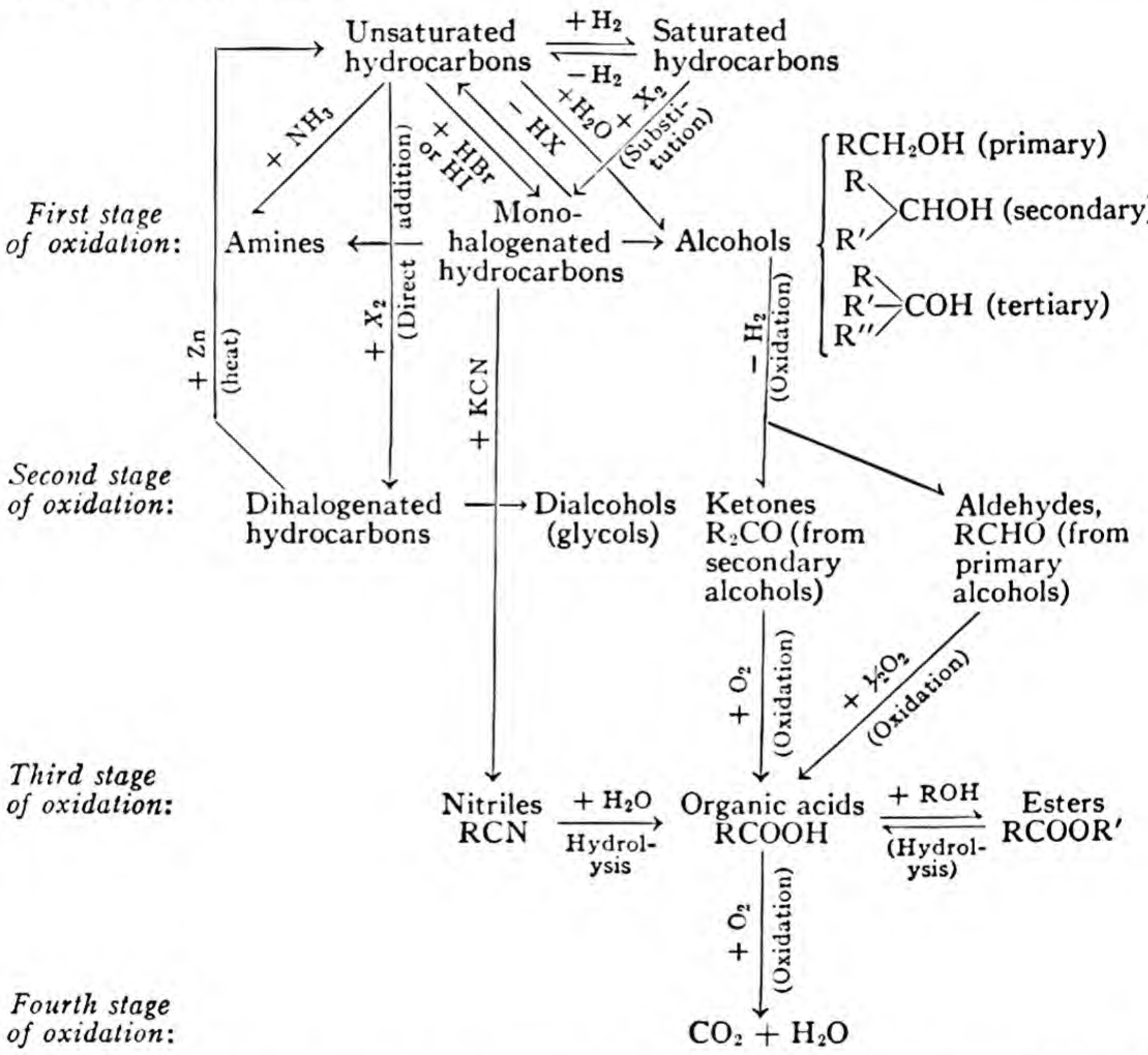
Reactive Atom or Group	*Name of Group*	*Class of Compounds*	*Formula of Methyl Compound*	*Name of Methyl Compound*
—Cl		Organic chlorides	CH_3Cl	Methyl chloride
—Br		Organic bromides	CH_3Br	Methyl bromide
—OH	Hydroxyl group	Alcohols and phenols	CH_3OH	Methyl alcohol (methanol)
$-NH_2$	Amino group	Primary amines	CH_3NH_2	Methylamine
>NH	Imino group	Secondary amines	$(CH_3)_2NH$	Dimethylamine
>N—		Tertiary amines	$(CH_3)_3N$	Trimethylamine
$-NO_2$	Nitro group	Nitro compounds	CH_3NO_2	Nitromethane
H—>CO	Aldehyde group	Aldehydes	CH_3CHO	Acetaldehyde
>CO	Ketone group	Ketones	$(CH_3)_2CO$	Dimethylketone (acetone)
—CN	Cyanide group	Nitriles	CH_3CN	Acetonitrile
—C=O, \OH	Carboxyl group	Organic acids	CH_3COOH	Acetic acid
—C=O, \OR *		Esters	CH_3COOCH_3	Methyl acetate

* R represents any hydrocarbon radical, such as CH_3—, C_2H_5—, or C_6H_5—.

464. Some Typical Reactions

Everyone who expects to do any reading in the field of organic chemistry should devote enough attention to the table just given to become familiar with the chief reactive atoms and groups, and with the class of compounds that each determines. A course in organic chem-

istry usually consists almost entirely of a survey of the principal chemical reactions entered into by the compounds of each class, with some allowance made for differences between the behavior of the aliphatic and aromatic compounds. We shall need to be content with a diagram that shows some of the chief ways in which the members of any one class of compounds may be converted into the corresponding members of any other. Half arrows, ⇀, indicate reactions for which a *catalyst* is ordinarily needed. R or R′ stands for any aliphatic or aromatic hydrocarbon radical.



Notice particularly the formation of esters by the reaction of organic acids with alcohols:

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \rightleftharpoons \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

Since reactions of this type (*esterification*) are always reversible and consequently incomplete, steps must often be taken to remove the

ester or the water that the reaction produces, thus hindering the reverse reaction and so insuring that the forward reaction shall be more nearly complete than it otherwise would be.

In addition to the reactions shown in our diagram there are, of course, dozens of others of great importance and many types of compounds that we have not even mentioned. Our purpose is served if the reader will spend a little time in examination of the reactions indicated. The chapter just completed will have given him an idea of how organic compounds are classified, first into four great divisions (§ 454), according to the kind of carbon skeleton that the molecule possesses, then into smaller classes, in all four divisions, according to the reactive atoms and groups that happen to be attached to the carbon skeleton. We have given a glimpse of how structural formulas are determined and what sort of reactions may be employed in transforming one class of organic compounds into another. In the following chapter we shall see how this knowledge has been applied in the synthesis of a multitude of useful products in many different fields of life and industry.

Technical Words

Carbon skeleton—a group of carbon atoms, arranged and interconnected in a definite manner, and serving as the framework of an organic molecule.

Aliphatic compounds, p. 521. **Alicyclic compounds**, p. 521.

Aromatic compounds, p. 521.

Carbocyclic compounds—a general term, including alicyclic and aromatic compounds.

Heterocyclic compounds, p. 521. **Graphic formula**, p. 296.

Structural formula, p. 296.

Saturated compounds—compounds that fail to combine with hydrogen or the halogens by direct addition (except occasionally when an aromatic ring becomes an alicyclic ring, by catalytic addition of hydrogen or halogen).

Unsaturated compounds—compounds that combine directly with hydrogen or the halogens, even in the absence of a catalyst. This is evidence of the presence of one or more double or triple bonds.

Paraffin hydrocarbon, p. 526. **Olefin**, p. 528.

Isomeric compound or **isomer**, p. 527.

Polymerization, p. 529. **Polymer**, p. 529.

Dimer—a product obtained by the direct union of two identical simple molecules (the first stage in polymerization).

Reactive or **functional atom** or **group**—an atom or group that determines the reactions of a particular organic compound or class of compounds.

Ortho compound—an aromatic compound in which two substituting groups or atoms are attached to adjacent (1,2) carbon atoms.

Meta compound—an aromatic compound in which two substituting groups or atoms are attached to neighboring, non-adjacent (1,3) carbon atoms.

Para compound—an aromatic compound in which two substituting groups or atoms are attached to opposite (1,4) carbon atoms.

Condensed rings—rings of carbon atoms that have two or more atoms in common.

Methyl group—the group CH_3—.

Ethyl group—the group C_2H_5—. Observe that the saturated aliphatic groups are named from the corresponding paraffin hydrocarbons (§ 458), but with the ending *-yl* instead of *-ane.*

Phenol—any compound containing one or more hydroxyl groups, attached to a benzene ring; also the simplest of such compounds, C_6H_5OH.

Ester—a substance characterized by the group —COOR, in which R is any hydrocarbon radical.

Esterification—the production of an ester (and water) by reaction of an organic acid with an alcohol. The reverse reaction is an example of hydrolysis.

Condensation—a reaction in which new carbon-to-carbon linkages are produced. Polymerization (reactant molecules identical) is a special case.

Synthesis—any reaction in which elements combine to form a compound or in which simple molecules react to form more complex molecules.

Exercises

1. Explain why we now prefer to say that carbon has a *covalence* rather than a valence of 4.

2. How many electrons are involved in a single covalent bond? What is true of their spin?

3. Work out the ten different possible ways of connecting five carbon atoms (§ 453) by single bonds. Determine whether the total number of bonds not used in connecting the carbon atoms is the same for all ten arrangements of the carbon atoms.

4. Write graphic formulas for the four hydrocarbons that contain a carbon skeleton of four atoms, linked by single bonds.

5. A liter of the vapor of methyl ether, recalculated to standard conditions, weighs approximately 2.05 grams. Analysis shows that this compound contains 52.2 per cent carbon, 13.1 per cent hydrogen, and the remainder oxygen. Find the molecular weight of methyl ether and the weight of each element in the molecular weight. Then compare with atomic weights of the elements to determine the molecular formula.

6. From the molecular formula of methyl ether, derived in the preceding exercise, deduce a graphic formula consistent with two facts: (1) phosphorus trichloride does *not* introduce an atom of chlorine, in the place of an atom of oxygen and one of hydrogen; (2) each molecule of the ether, on being hydrolyzed, yields two *identical* molecules (of methyl alcohol), thus indicating that the ether molecule possesses a symmetrical structure.

7. What name would be given a compound in which two hydrogen atoms, originally attached to the two end carbon atoms of propane, have been replaced by bromine?

8. What is the name of the compound obtained by replacing all six of the hydrogen atoms of ethane by chlorine atoms?

9. Write structural formulas for all possible pentanes that do not contain closed rings of atoms.

10. Determine how many different monochlorobutanes can be obtained by substituting a chlorine atom for a hydrogen atom of butane, in all possible positions. (Two positions are to be regarded as identical if one can be brought into the position of the other by turning the molecule end for end or upside down, or by bending any of the carbon-to-carbon links through an angle.)

11. How many different isomeric propylenes exist?

12. Write a graphic formula for 2-hexene, and explain why this compound is identical with 4-hexene.

13. Write an electronic formula (§ 247) to show the manner in which water molecules become linked in forming an associated molecule.

14. Write a structural formula for 1,2-dimethyl-6-chloronaphthalene.

15. Assume the benzene ring to be a regular hexagon, with all six carbon atoms in equivalent positions. Then determine how many different trichlorobenzenes can be produced from *ortho*-dichlorobenzene. Similarly, how many trichlorobenzenes can be prepared from *meta*- and from *para*-dichlorobenzene?

16. The xylenes are dimethylbenzenes. Write structural formulas for *meta*-xylene and *para*-xylene.

Chapter 34

SOME FAMOUS SYNTHESES

465. Raw Materials for the Organic Industries

Since prehistoric times many industries have been based on organic raw materials, given us ready-made by nature. Five chief groups of such raw materials are now important:

1. *Fibrous plant materials*, including wood, cotton, linen, etc. *Cotton and linen are nearly pure cellulose*, and wood is roughly half cellulose, in association with other organic materials.

2. *Non-cellulosic plant materials*, including hydrocarbons, such as turpentine and rubber; organic acids, such as citric and tartaric acids; and nitrogenous compounds, such as quinine, cocaine, and plant proteins.

3. *Animal products*.

4. *Coal*, which is a very complex mixture of compounds, derived from the cellulose and other compounds in the prehistoric plant material from which the coal was derived.

5. *Petroleum and natural gas*, which consist chiefly of *hydrocarbons* that have been accumulated in the depths of the earth by processes that are still very incompletely understood, but doubtless involved the action of heat and pressure on plant material (perhaps often consisting chiefly of algae and other microscopic organisms). Petroleum from the eastern part of the United States is nearly altogether a mixture of saturated hydrocarbons of the paraffin series (§ 458). That from California includes a considerable proportion of oxidized and polymerized products (p. 529), left behind as *asphalt* when the petroleum is distilled. The petroleum from Texas and neighboring states is roughly intermediate in chemical composition between the Pennsylvania and California types.

In cracking petroleum for the production of gasoline (§ 460) about 7 or 8 per cent of the material is converted into gaseous products, including the paraffin hydrocarbons methane, ethane, and propane,

and the unsaturated hydrocarbons ethylene, propylene, and butylene. As much as 14,000,000 tons of these gaseous by-products are produced every year in the United States alone. Unfortunately their chief present use is as fuel gas, in heating petroleum stills and cracking units. A recent development is the polymerization of the unsaturated gaseous hydrocarbons to produce annually (1940) as much as a million gallons of liquid motor fuel, which is of such high anti-knock quality that it is especially suited to aviation. A small part of the unsaturated gaseous hydrocarbons serve as raw material in the synthesis of other classes of organic compounds.

466. The Cellulose Industries

The *manufacture of paper* and the *textile industries* represent enterprises in which the cellulosic fibrous material produced by nature is merely purified.

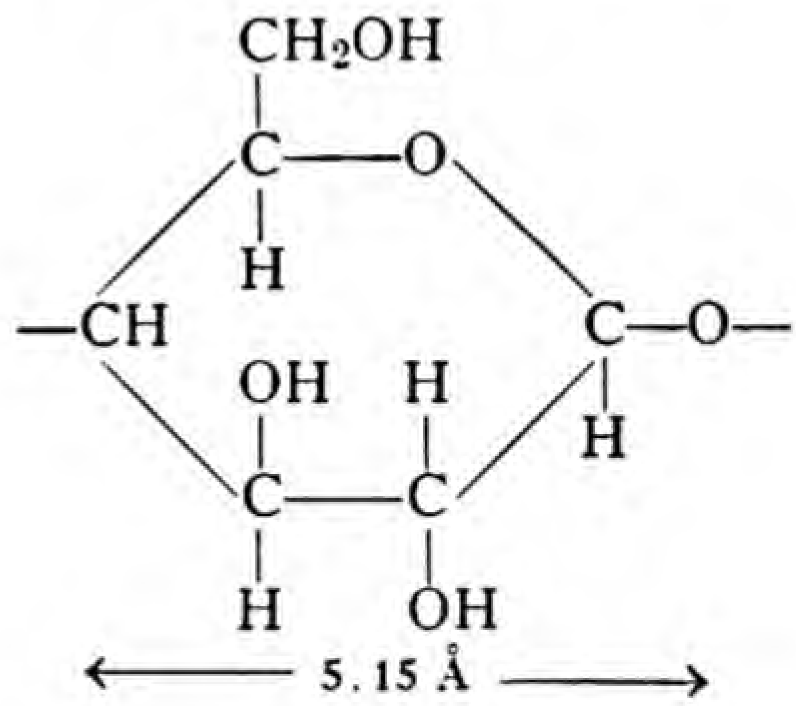
Most paper is now made from paper pulp, obtained by digesting wood chips, under pressure, with a hot solution of calcium acid sulfite, sodium hydroxide, or sodium sulfide. The non-cellulosic organic compounds in the wood are thereby hydrolyzed and dissolved, thus freeing the cellulose fibers (still very impure) for a felting process, in which they interlock to form a sheet of paper. Newspapers contain a considerable proportion of wood fibers, torn from the wood by revolving grindstones, without any chemical treatment whatever. (Ex. 1.)

A nearly pure form of cellulose, often termed *alpha-cellulose*, is made by further purifying sulfite-treated wood fibers, by oxidizing and dissolving impurities, in treating the fibers with chlorine. Alpha-cellulose and cotton linters (the short fibers or fuzz from cottonseed) serve as a raw material in the production of *rayon*. The cellulose is first treated with a solution of sodium hydroxide in the presence of carbon disulfide. A soluble product (*viscose*) is thus obtained, which is dissolved in water and forced through fine openings into dilute acid. This reconverts the dissolved viscose into nearly pure cellulose, $(C_6H_{10}O_5)_n$, and coagulates the solution as fine threads, which are stretched, dried, twisted, and reeled, later to be dyed and woven into textiles. The same material (nearly pure cellulose), formed into sheets instead of threads, bears the trade-name *cellophane*.

In still another group of industries cellulose is chemically altered by destructive distillation (yielding charcoal, acetic acid, and acetone as chief products). Finally, we have a group of industries in which cellulose reacts with acids or acid anhydrides to form esters. (Ex. 2, 3.)

467. Cellulose Esters

To understand what happens in the production of cellulose esters we need only note that cellulose is chemically an *alcohol*, since it possesses reactive hydroxyl groups. The cellulose molecule is composed of an indefinite number of the groups



linked together to form a long chain. A number of such chains, laid down side by side, and cross-linked through hydrogen bonds (§ 272), constitute the cellulose fiber. (Ex. 4, 5.)

When cellulose is momentarily treated with a slightly diluted mixture of nitric and sulfuric acids, a certain proportion (about $\frac{2}{3}$ to $\frac{3}{4}$) of its hydroxyl groups are converted into nitrate groups $—ONO_2$. The product, *pyroxylin* (often called cellulose trinitrate, or, less properly, "nitrocellulose"), still has the fibrous structure of cellulose, but is soluble in a mixture of alcohol and ether and in a wide range of other organic solvents. *Cellulose nitrate lacquers* (the chief automobile finishes since 1930) are solutions of pyroxylin in esters and alcohols, thinned with hydrocarbons, and carrying finely dispersed inorganic pigments. The material known by the trade-names Celluloid, Pyralin, etc., consists of pyroxylin, rendered plastic by camphor. Its chief disadvantage is its extreme flammability. Professional motion picture film and most film for still pictures are made of this material.

When cotton is treated with a mixture of concentrated nitric and sulfuric acids, or when a somewhat diluted mixture of acids acts on cotton for some time, the nitration proceeds past the pyroxylin stage and we get a more highly nitrated product, still fibrous, but no longer soluble in a mixture of alcohol and ether. This is *guncotton*, which burns harmlessly, though almost instantly, if ignited, but explodes when violently struck or when subjected to a detonator (p. 433). (Ex. 6.) About $\frac{5}{6}$ of the hydroxyl groups in cellulose have been replaced by nitrate groups, in most samples of guncotton.

Nobel (1867) discovered that guncotton dissolves in warm nitroglycerin, chemically called glycerol trinitrate, $C_3H_5(ONO_2)_3$, itself an explosive (§ 381). The result is a gelatinous mass, which is the basis of modern smokeless powder. Smokeless powder and guncotton belong to the relatively slow-burning class of explosives known as *propellants*, which are used to fire projectiles from guns. (Ex. 7.)

In photographic films for X-ray work and amateur motion pictures the plastic material is *cellulose acetate* rather than cellulose nitrate. It is usually produced by the interaction of a mixture of acetic acid, CH_3COOH, and acetic anhydride, $\begin{matrix} CH_3CO \diagdown \\ \qquad\quad O \\ CH_3CO \diagup \end{matrix}$, on highly purified cellulosic material, in the presence of a catalyst. Cellulose acetate may be dissolved in acetone and in many different alcohols and esters, and with suitable plasticizers may be converted into film, lacquers, and textile fibers. Cellulose butyrate, and mixtures of this with cellulose acetate, are also used as plastics, in certain special applications. (Ex. 8.)

468. Phenolic Plastics

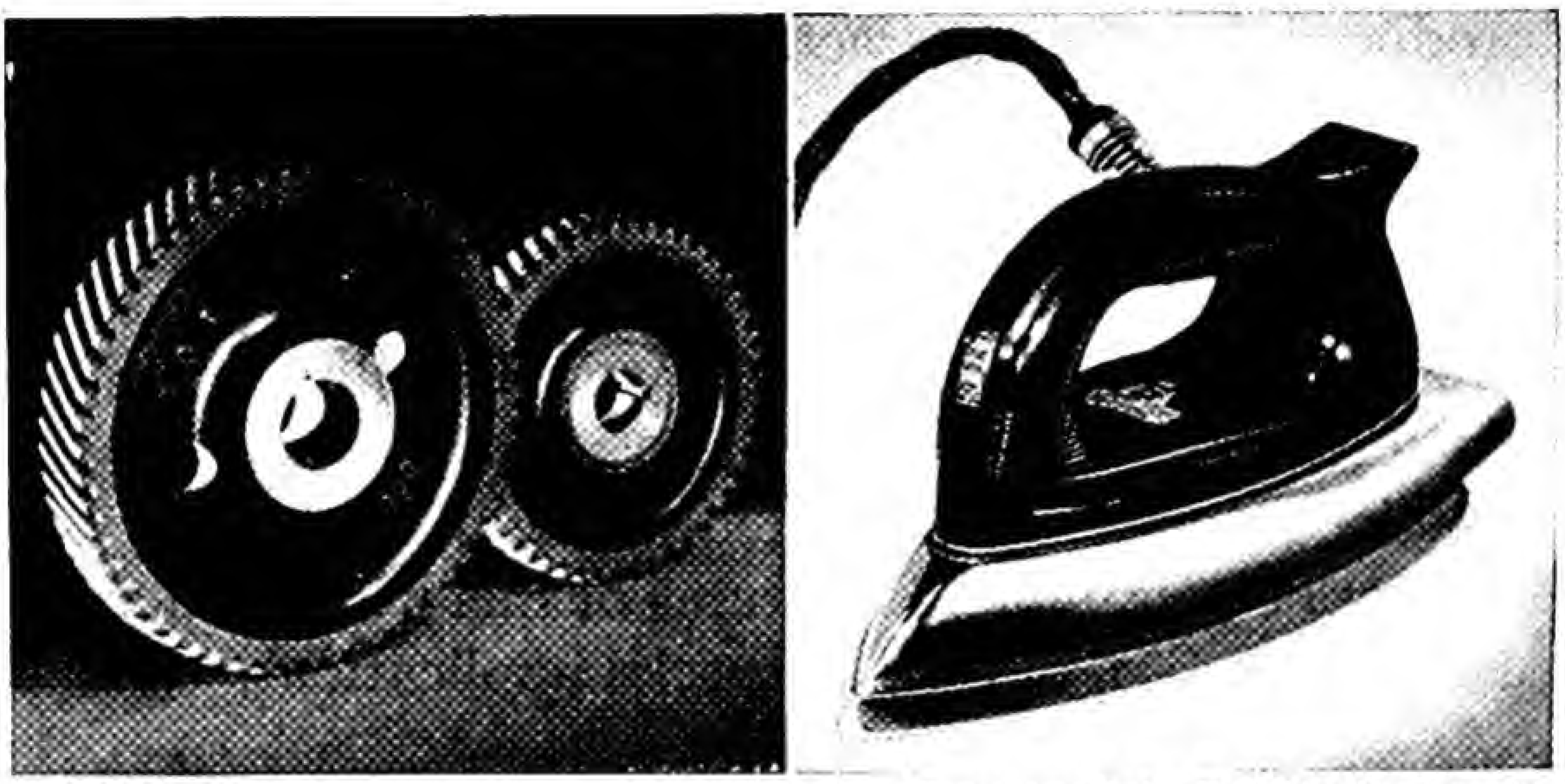
A *plastic* is a material that may be given a desired shape by pressure, and that then retains that shape. Prehistoric man fashioned vessels of plastic clay and discovered that they could be permanently hardened by being strongly heated in a furnace. Natural organic plastics known to prehistoric man included beeswax, various resins secreted by trees, and *bitumen* (a black, mineral pitch). *Amber* is a fossil resin which becomes slightly plastic when strongly heated in a bath of glycerol.

Synthetic chemistry has produced many plastics quite unknown in nature. Those that are softened by heat are said to be *thermoplastic*. Certain of these are also *thermosetting*—a term used to indicate that the material, after being softened or melted by heat and forced or poured into a heated mold, undergoes a chemical change in the mold, being thus rendered permanently infusible, below temperatures at which it actually chars. Shellac, the product of the lac insect of India, is thermosetting, though the setting takes place very slowly.

In sharp contrast with the derivatives of rubber and cellulose are numerous other plastics which chemists have learned how to synthesize from relatively simple molecules. The simple molecules are caused to combine with one another to form long chains, which are then inter-

locked by cross connections. The result is a giant molecule, or a confused network of interlacing molecules, which is difficult to melt and insoluble in solvents not sufficiently reactive to tear it apart and so bring it into solution by slow degrees.

The first plastics to be produced in the manner just described were those developed by Baekeland, a Belgian-American chemist, about 1900. They are formed by the reaction of phenol, C_6H_5OH, with



Courtesy of the Bakelite Corporation

FIG. 143. Phenol-formaldehyde plastics: a laminated gear and a flatiron handle.

formaldehyde, HCHO, in the presence of a catalyst. Two steps are often involved:

1. When an acid catalyst is employed, with a very limited amount of aldehyde, a soft, fusible resin is produced.

2. When the fusible resin is mixed with a further quantity of aldehyde and pressed in a heated mold, a chemical reaction soon takes place, in which the resin becomes permanently hard and infusible.

Molded phenolic resins, prepared as just described (trade-names: Bakelite, Durez, Textolite, Resinox, etc.), are distinguished by low cost, resistance to heat, water, and chemicals, ready moldability, and good insulating qualities. They are not readily obtained in other than dark shades. Commonly about 40 per cent finely ground wood (wood flour) is used as a filler to decrease cost and increase tensile strength. Sometimes the wood flour is replaced by mineral fillers, such as asbestos fiber or mica. The result is a *heat-resistant* product, usable up to temperatures of about 230°C, in plugs for electric irons or in handles for kitchen utensils. By using fiber glass (§ 488) as a filler, phenolic resins may be given greatly increased resistance to blows or sudden shocks. By using graphite as a filler, resins may be prepared that serve as frictionless rollers or casters.

Observe two different methods for molding such materials, shown in Fig. 144.

Cast phenolic resins, instead of being permanently hardened by being pressed in steam-heated molds, are first *melted* and poured into molds, then hardened by heating. In preparing these resins an *excess of formaldehyde* is used, with an alkaline catalyst. The first result is

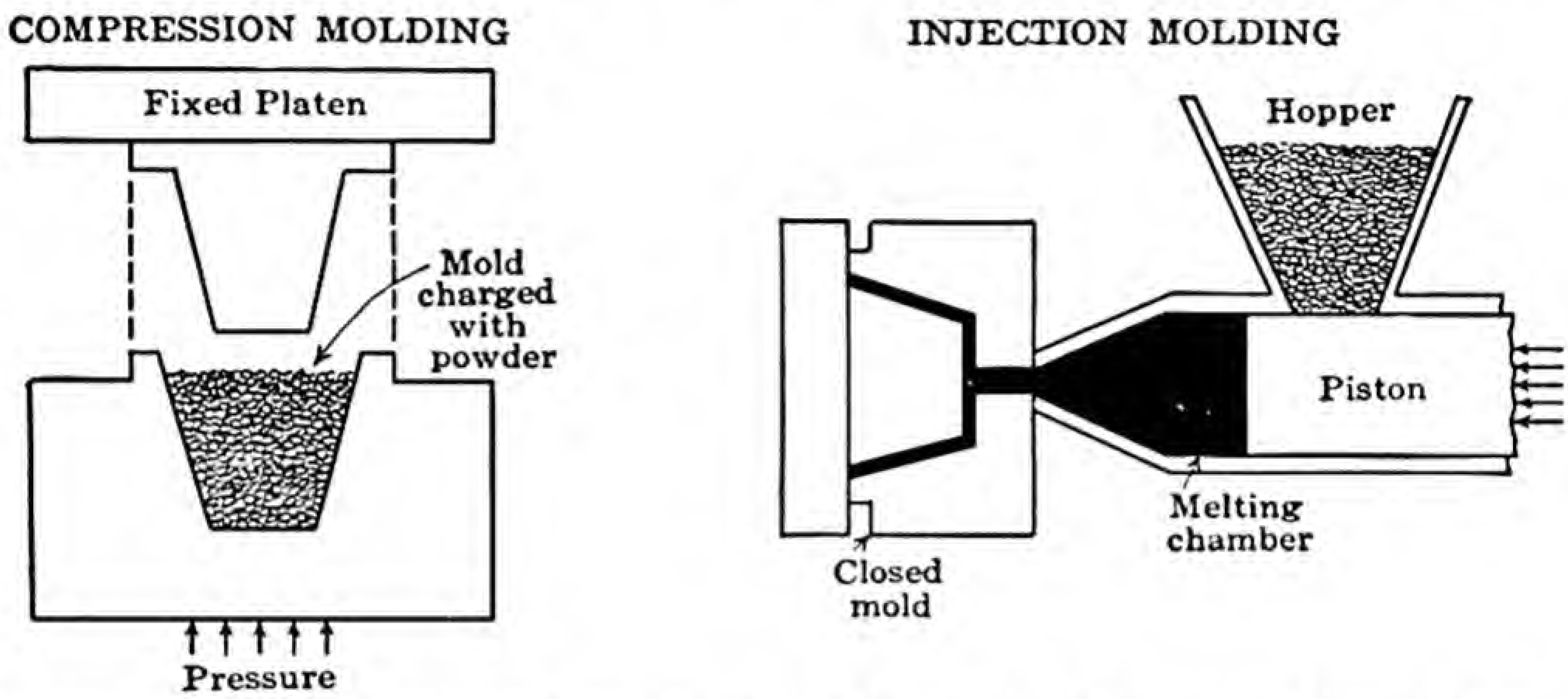
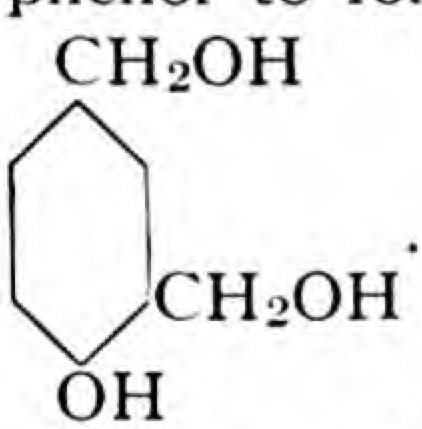


FIG. 144. Two ways of molding plastics. The method shown on the left is applied when the material must be held in the heated mold for a certain period of time while the thermosetting process takes place. The method on the right is faster and more nearly continuous. In addition, plastics may be shaped by continuous extrusion through a die, or may be extruded or rolled into sheets.

the condensation of two aldehyde molecules with one molecule of phenol to form the sodium or potassium salt of the phenol-alcohol,



. This polymerizes to form water-soluble products which, on being acidified and then freed from water by distillation in a vacuum, yield a water-soluble, transparent, low-melting resin. This may be melted, cast in glass or lead molds, then permanently hardened by heating at the comparatively low temperature of 80°C. The water set free in the final reaction renders the material opaque; but by the addition of glycerol, $C_3H_5(OH)_3$, or some other hygroscopic material, the size of the droplets of separated liquid may be reduced and the material rendered translucent or comparatively transparent.

Even in the complete absence of fillers, cast phenolic resins are strong and both heat- and water-resistant; they can be readily turned and machined, and can be dyed in light colors and pastel shades by

means of dyes which recent research has produced especially for this purpose. They are used for bright-colored small objects such as necklaces, ash trays, electric shavers, toothbrush handles (trade-names: Catalin, Phenalin, Resinoid, Monsanto Cast Phenolic).

Phenolic resins, before being permanently hardened by heat, may be used as adhesives in the preparation of layered products. Gears and panels are commonly made of tough sheets of fabric, criss-crossed, then bonded together with phenolic resins, which are given a permanent set in a steam-heated press.

Plywood is made by bonding paper-thin sheets of wood. It may be made as strong as an equal weight of steel. Its extra thickness, as compared with steel or light alloys of the same strength, is a great advantage in making it less subject to buckling under stress. For airplane structures, plywood has the advantage of presenting a smooth surface, free from rivets or welded joints.

When phenolic resins capable of being hardened by heat are dispersed in suitable solvents they form *lacquers*, widely used for covering fine copper wire with a thin insulating film or for giving wood or fabric an oil-proof or water-proof coating. Lacquer films may be given extra flexibility or plasticity by being intermingled with a *plasticizer*. Phenolic resin lacquers, applied by spraying, thicken by evaporation of the solvent and are then permanently hardened by baking in an oven or by being exposed to radiation from banks of infrared lamps. (Ex. 9.)

469. Casein Plastics

Casein is a protein (§ 358) which makes up most of the clot or curd of curdled milk. As in other proteins, certain groups,

$$\begin{array}{c} \mathrm{R} \\ | \\ \mathrm{—NH—C—CO—} \\ | \\ \mathrm{H} \end{array}$$

repeat in a chain-like structure. The group R may be an atom of hydrogen, or it may include rings and branched chains, together with reactive groups, which in unknown ways establish cross connections between neighboring chains.

When casein or the proteins of the soybean are heated with formaldehyde, the formaldehyde establishes new cross linkages between the protein molecules. The result is a horn-like solid marketed as sheets, tubes, or rods. It is not thermoplastic, but it is useful because it can

be easily stamped into buttons or worked with woodworking tools. It is much more resistant than the original protein to disintegration by reagents or penetration by water. (Ex. 10.)

Casein plastics are cheap, strong, and readily dyed, but cannot readily be molded, and they twist or warp somewhat with changing moisture content. They are used chiefly for small objects, such as buttons and buckles, which do not need to be accurately dimensioned or perfectly flat (trade-names: Ameroid, Galalith).

470. Urea Plastics

Urea, $\mathrm{C{\overset{\displaystyle\nearrow NH_2}{\underset{\displaystyle\searrow NH_2}{O}}}}$, may easily be made to react with formaldehyde, HCHO, which serves to link two molecules of urea together through an intervening carbon atom furnished by the formaldehyde:

$$\mathrm{CO}\begin{smallmatrix}\nearrow NH_2\\ \searrow NH_2\end{smallmatrix} + \underset{\text{Formaldehyde}}{\overset{\overset{\displaystyle O}{\|}}{CH_2}} + \mathrm{CO}\begin{smallmatrix}\nearrow NH_2\\ \searrow NH_2\end{smallmatrix} \rightarrow \mathrm{NH_2{-}CO{-}NH{-}CH_2{-}NH{-}CO{-}NH_2 + H_2O}$$

Then other molecules of urea may be added, building up long chains which cross-link to form a network. Thus we obtain an insoluble, nearly infusible plastic.

The *urea-formaldehyde* plastics are widely used in molding objects that must be transparent or brightly colored, odorless and tasteless, of high tensile strength, resistant to solvents, and not easily scratched. With cotton linters or purified wood pulp, serving as a filler, they imitate ivory in radio cabinets, clock cases, umbrella handles, bottle caps, buttons, and a multitude of other objects (trade-names: Plaskon, Beetle). The urea plastics are unfortunately rather easily shattered by a blow unless reinforced by fiber glass or long-fibered cellulose.

471. Vinyl and Vinylidene Plastics

Other useful groups of plastics have been produced from *vinyl acetate, vinyl chloride, vinyl alcohol, and vinylidene chloride:*

$$\underset{\text{Vinyl acetate}}{\begin{array}{l}\mathrm{CH{=}CH_2}\\ |\\ \mathrm{OCCH_3}\\ \|\\ \mathrm{O}\end{array}} \qquad \underset{\text{Vinyl chloride}}{\begin{array}{l}\mathrm{CH{=}CH_2}\\ |\\ \mathrm{Cl}\end{array}} \qquad \underset{\text{Vinyl alcohol}}{\begin{array}{l}\mathrm{CH{=}CH_2}\\ |\\ \mathrm{OH}\end{array}} \qquad \underset{\text{Vinylidene chloride}}{\begin{array}{c}\mathrm{C{=}CH_2}\\ \swarrow\ \searrow\\ \mathrm{Cl}\quad\ \mathrm{Cl}\end{array}}$$

The presence of a double bond permits these molecules to polymerize to form long chains, which may be altered by partial hydrolysis, thus replacing some of the chloride or acetate groups by hydroxyl groups. The material will then polymerize, hydroxyl groups on any chain reacting with chloride or acetate groups on neighboring chains, thus linking each chain with its neighbors; or an aldehyde may be used

Courtesy of E. I. du Pont de Nemours & Co.

FIG. 145. A tough, elastic sheet of Butacite (a vinyl plastic) which is the inner layer of safety glass. The sheet is cross-ribbed with faint depressions to keep it from sticking to adjacent sheets, when the material is stacked. When pressed flat it becomes completely transparent.

to establish cross connections between neighboring chains. By *co-polymerizing* two or more different raw materials (for example, vinyl chloride, co-polymerized with vinyl alcohol) plastics may sometimes be produced that are superior to those made by polymerizing any single raw material. In this manner vinyl plastics have been prepared that are so adhesive, weather-resistant, and shock-resistant that they may be used to join sheet metal, as a substitute for soldering or riveting. (Ex. 11.)

Vinyl plastics may be applied to yield water-proof surfacing for cloth, metal, paper, and ceramic ware. Steel sheets coated with these films may be crimped, punched, or drawn without damaging the protective film. Other vinyl plastics withstand the hot acids of electro-

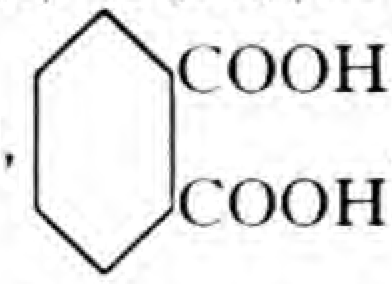
plating baths or replace tin in lining cans. They maintain their dimensions without shrinking, warping, or twisting with changes in temperature and humidity.

Vinyl plastics are resistant to penetration by water, and are odorless, tasteless, and non-toxic. When unplasticized, they are stiffer than most other thermoplastic materials. They are used in brightly colored drinking cups, trays, and boxes. As lacquers they are used as an insulating coating for wire (trade-names: Polyvinyl chloride or acetate, Vinylite). Suitably plasticized, they emerge as water-proof, oil-proof, and acid-proof cable insulation or may be spun into threads which may be woven into water-proof semi-elastic fabrics (Vinyon). A related vinyl polymer of high elasticity (Butacite) forms the cementing layer between the two thin outer layers of glass in "safety glass" for automobiles.

The recently developed *vinylidene plastics* differ from others in passing into a crystalline condition if kept warm for a short time. When the material is drawn through a small opening the crystalline fibers become oriented into nearly parallel positions. The result is a great increase in the strength, flexibility, and toughness of the material.

The vinylidene plastics are resistant even to concentrated acids and alkalies (except NH_4OH). In the oriented crystalline condition the material is remarkable for its toughness and flexibility, hence replaces rubber and copper in such applications as acid dippers, refrigerator coils, cores for wire rope, flexible tubing and small pipes (for siphoning acids or for delivering oil or gasoline). Flexibility combined with resistance to water and oil has led to the use of these plastics in washable seat covers for automobiles and buses (trade-name: Saran). Open-mesh Saran cloth makes an excellent weather-proof fly screen, and draperies woven of the same material can be cleaned without being laundered. Saran is superior even to copper in its ability to withstand being broken by repeated flexure.

472. Other Plastics

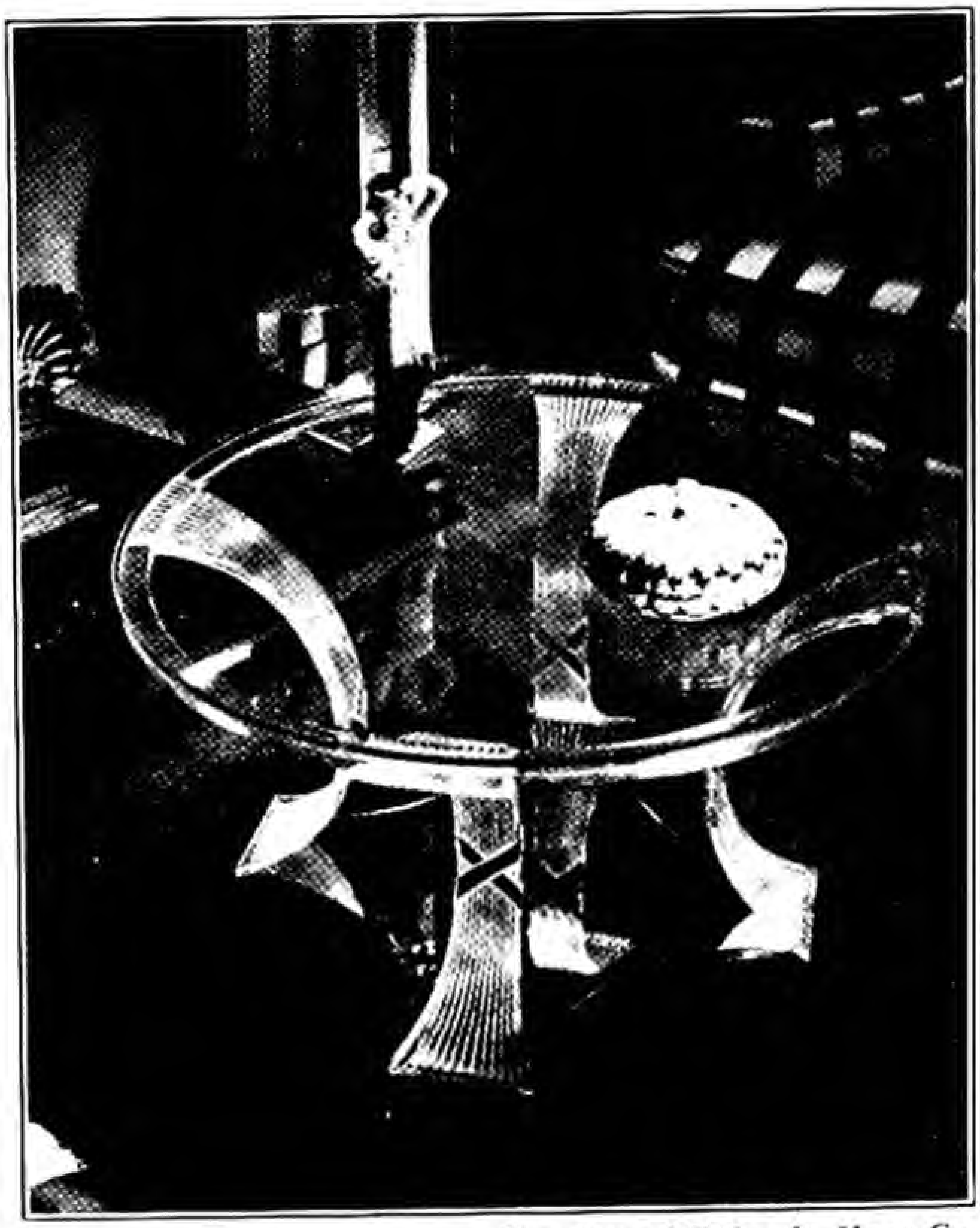
Still other plastics, having their own special uses, are well known in industry. *Alkyd resins* are made by reaction of polyhydroxy-alcohols, such as glycerol, $C_3H_5(OH)_3$, with polyprotic[1] organic acids, such as phthalic acid, 

, to form resinous esters possess-

[1] A polyprotic acid is one in which each molecule may yield two or more protons, in reactions with bases.

ing giant molecules of a confused pattern. Lacquers containing alkyd resins or polyvinyl resins are superior to the older cellulose nitrate lacquers, which they are tending to displace as automobile finishes. Their disadvantage has been that a car, on its fifth birthday, might still be so bright and new that it would be hard to sell the owner a more recent model.

The *polystyrene resins* (polymers of styrene, $C_6H_5CH{=}CH_2$) are distinguished by unusually low density (1.05) and by resistance to



Courtesy of Röhm & Haas Co.

FIG. 146. Plastics in the home. The table is an acrylic plastic, the chair is covered with a fabric of vinylidene or vinyl plastic, and objects on the table may be of any one of several other plastic types.

water, alkalies, and acids. They are used as washers in some recent closures for bottled chemicals, also in brightly colored dishes, trays, salad bowls, inkwells. Polystyrene resins can be molded to exact dimensions, which remain unaltered as the material ages (trade-names: Styron, Victron, Bakelite Polystyrene).

Methacrylate (or *acrylic*) resins have a high index of refraction. They will carry light around a corner, hence rods made of such material may be used by physicians to illuminate the throat and nasal passages.

A COMPARISON OF SYNTHETIC PLASTICS *

Plastics are numbered in order, from those in which the given property is highest to those in which it is lowest.

	Toughness (Impact Strength)	Flexural Strength	Tensile Strength	Color Stability	Resistance to Cold Flow	Resistance to Penetration by Water	Acid Resistance	Caustic Resistance	Solvent Resistance	Resistance to Dimensional Change on Aging	Resistance to High Temperature	Non-flammability	Heat Insulation	Specific Volume (Reciprocal of Density)	Hardness	A. C. Loss Factor	Resistivity	Dielectric Strength (A.S.T.M. ⅛" Inst.)	Moldability Around Inserts
Phenolic: general purpose	10	3	3	7	1	6	3	4	1	4	2	3	2	8	5	10	7	4	1
Phenolic: low-loss	8	3	7	7	1	3	4	4	1	2	3	1	7	12	3	4	3	3	1
Phenolic: heat-resistant	10	4	8	7	1	3	4	4	1	1	1	1	7	13	2		8	8	1
Phenolic: acid- and alkali-resistant	11	6	8	7	1	4	2	3	1	5	3	2	2	5	4			7	2
Phenolic: shock-resistant	2	1	5	7	1	7	4	5	1	6	3	4	3	10	5		9	8	1
Phenolic: transparent	7	1	3	7	1	4	2	3	1	5	3	2	2	6	4	7	5	6	2
Urea	9	1	1	1	2	9	4	4	1	7	7	5	5	11	1	9	4	1	3
Polystyrene	7	4	7	5	4	1	1	1	3	3	6	6	1	1	6	1	1	2	5
Cellulose-acetate	4	6	9	4	8	11	4	6	3	9	5	6	4	7	9	8	6	5	4
Aceto-butyrate	1	5	10	4	6	8	4	4	3	8	4	6	6	4	8	3			4
Ethyl cellulose	3	2	6	3	7	10	4	2	3	8	5	6	4	2	8	2	2	1	4
Methyl-methacrylate	6	1	4	2	5	5	2	2	3	8	9	6	2	3	7	5		2	5
Vinyl (no filler)	5	1	2	6	3	2	1	2	2	3	8	6	2	9	7	6	3	1	4
Vinylidene (crystalline)	1	1	1	2	2	1	1	1	2	1	7	6	1	12	1		1	1	5

* Courtesy of Bakelite Corporation.

Some brilliantly illuminated advertising signs, in which the words seem to stand out in letters of fire, are often made of this material. So are reflecting buttons for road signs or for markers for the edges of highways. The acrylic resins have considerable flexibility and are nearly shatter-proof (trade-name: Plexiglas). The transparent nose of a Martin bomber is formed by clamping the edges of a hot Plexiglas sheet to a form.

Some of the new synthetic resins, dispersed in water, may be applied as a paint that may be thinned with water and that will adhere even to wet surfaces. (Ex. 11.)

473. Nitrogenous Fibers

Fibers produced by animals (hair, wool, and silk, for example) are nitrogenous compounds called *keratins*—a class of proteins. Other proteins include albumen, muscle fiber, casein, and various groups of plant proteins. X-rays reveal that these nitrogenous fibers are in reality crystalline, with atoms definitely spaced and arranged, along a folded chain. When the fiber of hair, wool, or silk is stretched the X-ray pattern is completely altered, though the atoms still are regularly arranged. Evidence tends to show that links in the chain are

```
                                          —NH·····OC—
                                          /         \
folded back upon themselves, as in RCH             HCR, in which
                                          \         /
                                           CO——NH
```

NH and CO are weakly linked in some manner, as shown by the dotted line. The capacity of silk, wool, and hair to be considerably stretched when warm seems to be due to a rupture of the weak bond at the dotted line, the molecule then being pulled out straight. A bundle of such molecules constitutes a fiber. Hair is waved by stretching one side of the fiber more than the other. (Ex. 10.)

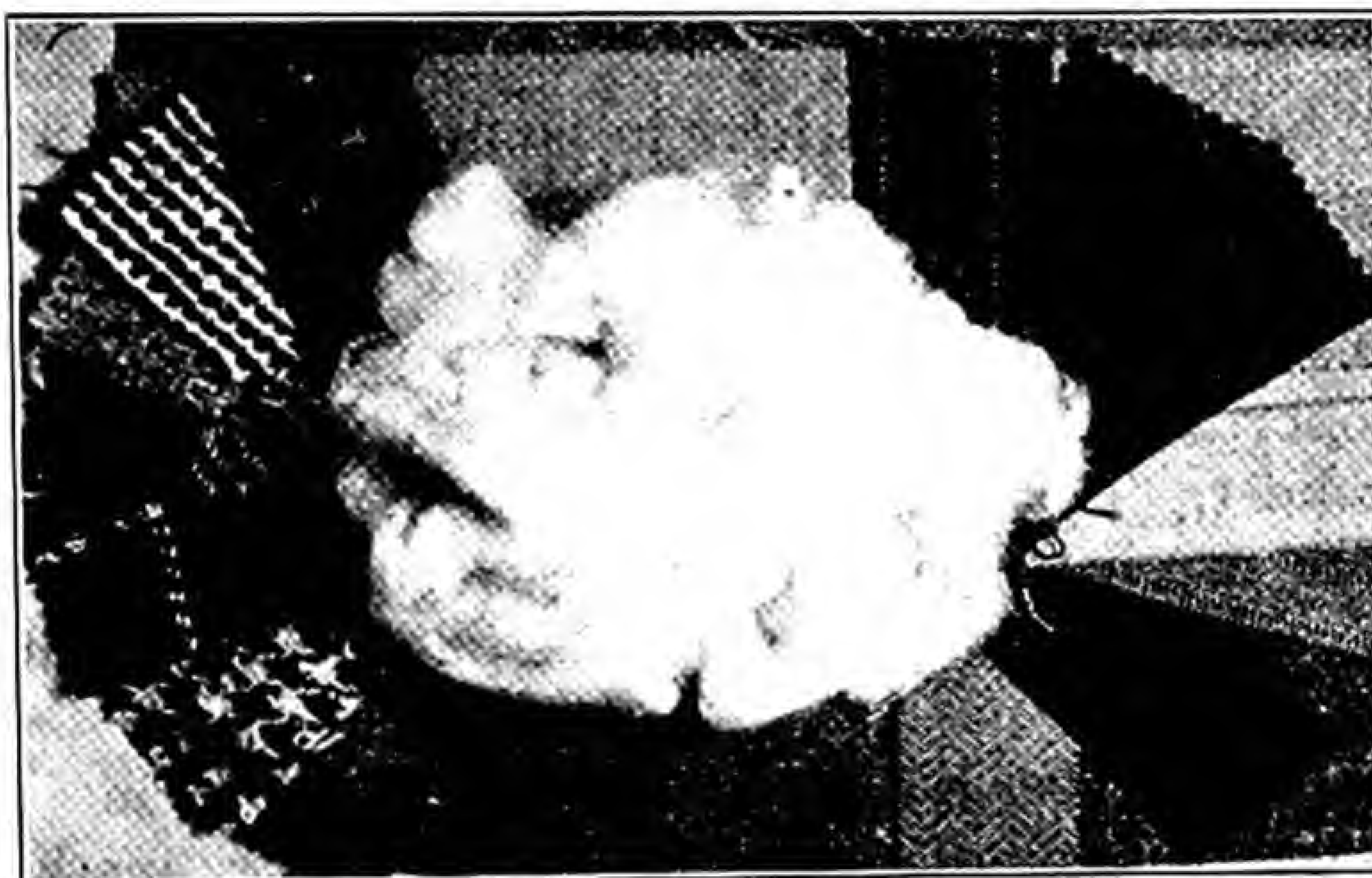
With this information at hand concerning the structure of the natural keratins, chemists have been able to synthesize nitrogenous fibers having some of the properties of wool and silk. In Italy a wool substitute (trade-name: *Lanital*) has been made from casein. In another process, feathers have been spun into fibers.

When phenol is reduced by hydrogen in the presence of a catalyst it adds five atoms of hydrogen and forms cyclohexanol,

$$\underbrace{CH_2(CH_2)_4CHOH}$$

When this is oxidized it forms adipic acid, $HOOC(CH_2)_4COOH$. Since

this has a carboxyl group, —COOH, on each end of the molecule, it can react with a diamine such as $H_2N(CH_2)_6NH_2$ (hexamethylenediamine), losing water, and forming long chains in which the group $—NH(CH_2)_6NH\cdot CO(CH_2)_4CO—$ is repeated an indefinite number of times. The first half of this group is obviously derived from the diamine and the second half from the adipic acid. By cross-linking the chains, through reaction with a further quantity of adipic acid we obtain *nylon*. By melting this product and extruding it through a die under tension, the fibers are pulled into parallel positions and the tensile strength is greatly increased.



U.S.D.A. Photograph by Purdy

FIG. 147. Textile fabrics woven of modified casein.

Nylon competes with silk in fineness, strength, and extensibility. Until the close of the recent war the army controlled the entire production, for parachutes, powder bags, glider towlines, and other uses. A similar product (Exton) is used for the bristles of toothbrushes. Paint brushes with tapered bristles of nylon fiber far outlast those with ordinary bristles.

Nylon has recently been produced with at least ten times the wearing quality of the best silk. Woven nylon fabrics may be given three-dimensional shapes by being cold drawn, then permanently set by treatment with hot fluids or steam. So we may presently have form-fitted garments, made without the aid of shears or tailor. (Ex. 13.)

474. Synthetic Elastomers

An elastomer is any natural or synthetic organic product with conspicuous toughness, and moderate or considerable extensibility,

resilience, and elasticity. The group includes natural rubber and many synthetic substances, some related to natural rubber and others very different.

Rubber is a hydrocarbon, $(C_5H_8)_n$, which is produced as a milky fluid called *latex* by several hundred different species of plants. Poor quality of the rubber and expense of collection prevent all but three of these plants from being worth considering as a commercial source of rubber. In recent peacetimes approximately 98 per cent of the American annual requirements of about 600,000 tons of new rubber were furnished by rubber plantations of the East Indies, producing rubber from the Hevea plant, which had been introduced from Brazil.

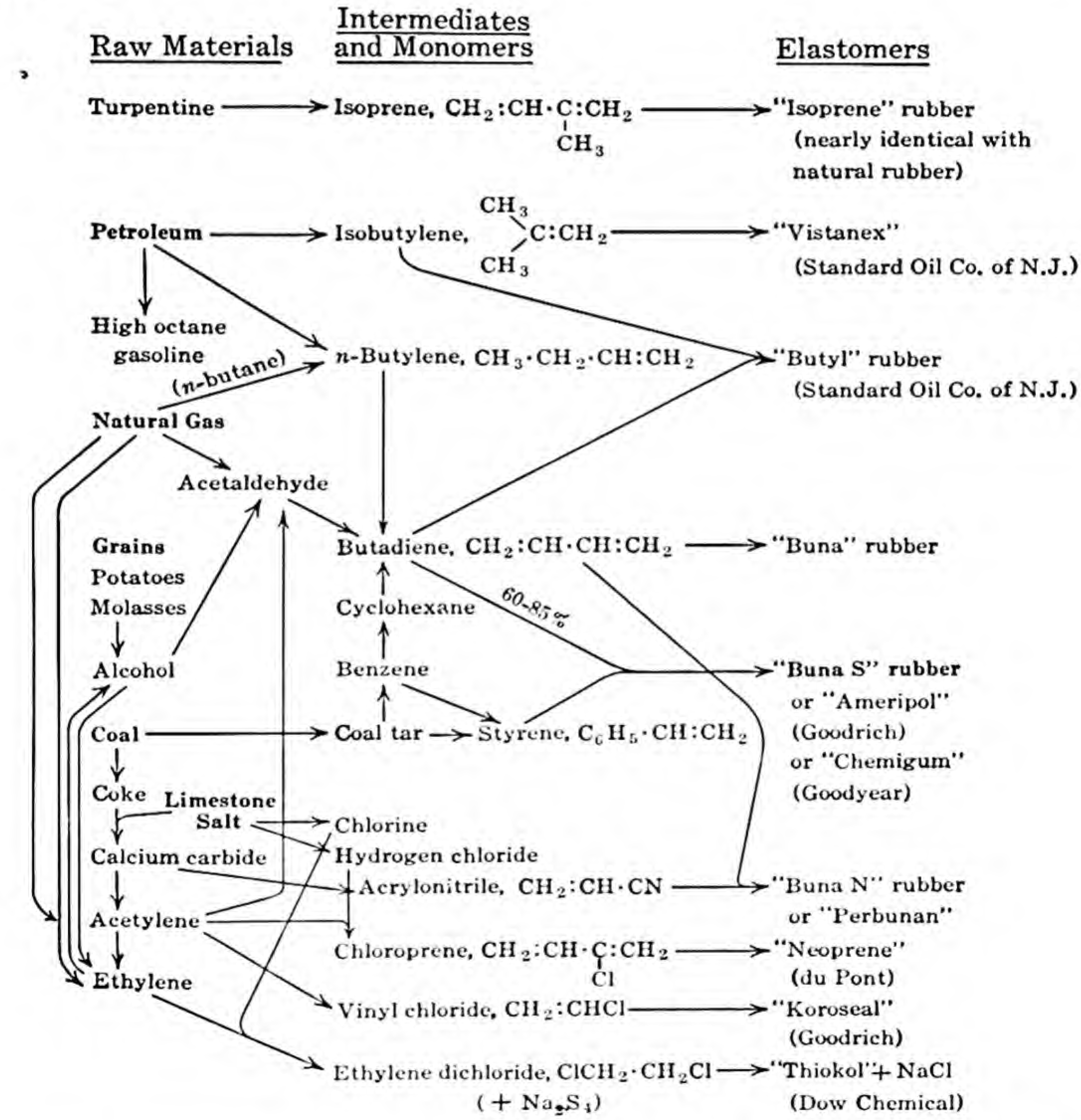
Raw rubber is soft and sticky in summer and almost as stiff as sheet iron in winter. Worse yet, it is weak and soon loses its elasticity. These difficulties were first overcome in 1839. Charles Goodyear, an American inventor, discovered that when crude rubber is heated with a small proportion of sulfur it becomes tougher, stronger, and less sensitive to heat. This was the first *vulcanizing* process. It was put to immediate use in the improvement of rubberized fabrics, which were even then being made, in spite of the poor quality of unvulcanized rubber. (Ex. 14.)

When natural rubber is destructively distilled the chief product is a colorless, extremely volatile liquid called isoprene (2-methyl-1,3-butadiene), $CH_2{:}CH\underset{\begin{array}{c}|\\ CH_3\end{array}}{C}{:}CH_2$ (m.p., $-120°C$; b.p., $34°C$).

It was long ago discovered that isoprene slowly thickens to a rubbery mass when heated or left standing in sunlight, or when hydrochloric acid is added. The product lacks the strength and wearing qualities of rubber, but is sufficiently like rubber to suggest that rubber itself is a polymer, formed by the linkage of isoprene molecules, to make a long chain. Commercial plantation rubber probably contains about 4000 of these "isoprene links" in a molecule.

Efforts to synthesize rubber by polymerizing isoprene met with little success in spite of earnest efforts begun in 1882. Other synthetic isomers, similar to rubber, were meanwhile invented and produced commercially, and were often found to be superior to true or isoprene rubber in resistance to oil and gasoline. Then true rubber was synthesized and in 1942 began to be produced commercially in a small plant using isoprene made from turpentine extracted from stumps of southern pine clearings.

Any "synthetic rubber" or rubber substitute (elastomer) which is to replace natural rubber must be derived from cheap raw materials, available in great quantities, since the American demand for elastomers is at least 800,000 tons a year. The best of those now known are produced by polymerizing simple unsaturated hydrocarbons or chlorinated hydrocarbons. The annexed table shows what raw materials are needed for producing the chief elastomers now known and what compounds serve as *monomers* (simple molecules that become linked together in the process of polymerization that produces the elastomer). (Ex. 15.)



The production of synthetic elastomers results in a competition of raw materials: petroleum, natural gas, grains, and coal. The most

useful of the synthetic elastomers, and the one on which we shall chiefly need to depend during the next few years, is the product known as *Buna S* rubber. This was developed in Germany, where a vital consideration was that it could be produced from coal and limestone, materials everywhere cheap and abundant. It can be vulcanized like natural rubber. It gives satisfaction in the treads of heavy-duty tires, but a considerable proportion of natural rubber, because of its superior resilience, is likely to be needed for the side walls; and natural rubber is superior to the synthetic product in retaining its resilience at very low temperatures.

Rubbers of American development that resemble Buna S in being based on butadiene (co-polymerized with other unsaturated hydrocarbons) are those known as *Ameripol* and *Chemigum*. They are superior to natural rubber in resistance to wear and abrasion or to the disintegrating action of oil and gasoline. Their chief defects when used in tires are the rapidity with which small cuts develop into large ones, and the extra heat they develop when repeatedly flexed.

Neoprene, the earliest successful synthetic elastomer of conspicuous extensibility, is superior to natural rubber in resistance to oil, gasoline, light, and heat. So it has had an important market since 1933, even in competition with natural rubber at a third or a fifth its price. It cannot be vulcanized, hence is not subject to the extreme alteration in properties that is secured by vulcanizing natural rubber. (Ex. 16.)

An entirely different group of rubber-like substances includes those produced by polymerizing vinyl chloride, $CH_2:CHCl$, in the presence of other substances. The products thus produced are as remarkable as rubber itself in being obtainable either as thin liquids, readily applied by spraying, or as extensible rubbery plastics, or rigid, tough solids.

Koroseal is another vinyl chloride polymer impressively like rubber in its general appearance, but superior to rubber in resistance to oil and gasoline and especially in being non-flammable. It is flexible and water-proof; it can be brightly dyed, and since about 1937 it has been familiar as bright-colored raincoats, umbrellas, shower curtains, and table covers. When used in food packaging, it can be sealed with a hot iron. Koroseal fibers, interwoven with nylon, make run-proof hose.

Thiokol is a rubber-like solid of very slight elasticity, resilience, or resistance to abrasion, but wonderfully resistant to oils and gasoline. It has been used for many years for the lining of the delivery hose of gasoline pumps, and for supports for the floating covers of gasoline tanks. A recent improvement is Thiokol latex, which enables Thiokol

to be applied by spraying, for example, in giving a protective coating to the submersion tanks of submarines. An important discovery is that Thiokol is serviceable as retreads, capable of lengthening the life of tires by 5000 to 10,000 miles.

The elastomers just described and others doubtless soon to appear will find their way into a multitude of uses in which natural rubber could never have been made to serve. During World War II the United States constructed plants to produce more than a million tons of synthetic rubber each year, about 80 per cent of which was accounted for by Buna S. This was more than two-thirds the world's production of natural rubber in 1941. The Buna S program, alone, called for an expenditure of $600,000,000. (Ex. 17.)

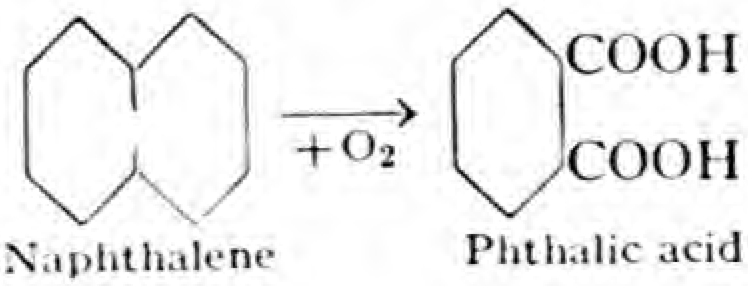
475. Synthetic Dyestuffs

Plants and animals supplied all the organic dyestuffs used by man from prehistoric times until the year 1856. The first synthetic dye was then produced by a young English student of chemistry, William Henry Perkin, then only seventeen. In an attempt to produce quinine, Perkin oxidized aniline with chromic acid. The result was a violet dye, which he christened mauve. In spite of his youth he followed up this discovery so vigorously that a small factory was soon in operation producing mauve for the market.

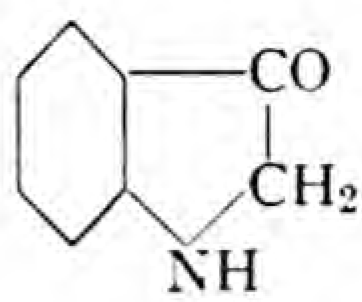
Other synthetic dyes almost immediately followed. The first of these was *alizarin* or *turkey red*, an important dyestuff previously obtained only from the madder plant. Many chemists in Germany, England, and the United States have contributed to the present industrial process, which starts with anthracene.

The next important natural dye to claim the attention of the synthetic chemist was *indigo*, a beautiful blue, produced by the indigo plant of the tropical Orient. For at least thirty-five centuries it had held a leading place in the dyer's art, and vast areas in India, Java, and China were devoted to its culture.

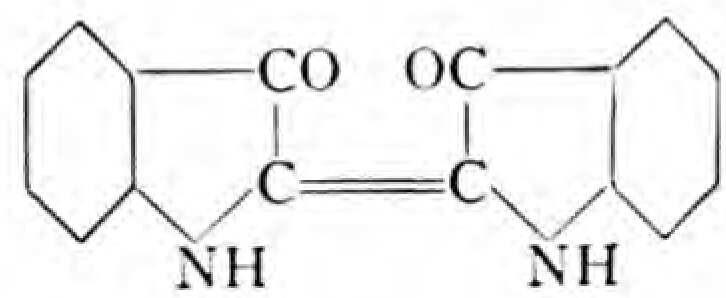
The synthetic production of indigo proved to be a very difficult problem. Many years were required to discover the structural formula of this substance, many more years to produce it on a laboratory scale, and further years and millions of dollars to develop methods that could be worked economically on a large scale. As the process at length was developed, naphthalene was oxidized, forming *phthalic acid:*



Then, by numerous separate steps a second ring, containing nitrogen, was built on to the benzene ring of the phthalic acid, thus producing *indoxyl:*



When this was agitated with air, oxidation occurred, removing hydrogen. The residues of two molecules were thereby linked to form a molecule of indigo:



Synthetic dyes have now largely replaced the natural products, and vast areas formerly devoted to the cultivation of indigo and madder are available for raising foodstuffs. Over 10,000 tons of synthetic indigo are now produced each year in the United States, and perhaps an equal amount abroad. The synthetic dyestuffs are purer and of more uniform quality than those produced in nature. In the years that have passed since the production of synthetic alizarin, thousands of other synthetic dyes have been made, and over a thousand are in actual use.

Rayon and cellulose acetate fabrics, and recently synthetic plastics, have called for new types of dyes and new methods of dyeing. Rapid progress has also been made in the art of applying dyes to fabrics, especially since 1920. Old processes have been simplified and new ones have been worked out that take advantage of suggestions offered by the structural formulas of the dyes themselves. When a fabric is woven of two different fibers (linen and silk, for example) the two may often be dyed in different colors by dipping the fabric into a mixture of two dyes, one suited to each fiber.

Although Germany held an almost complete monopoly of the manufacture of synthetic dyes before World War I, the chief industrial nations of the world are now able to meet most of their own dyestuff requirements.

476. Synthetic Perfumes and Flavors

Perfumes and flavors have been used since prehistoric times, and their production at present is a larger industry than most persons would imagine. The world—or the feminine half of it—is now thought

to consume at least two thousand tons of perfume each year, for which it pays many millions of dollars.

Many fruits and flowers owe their odor to simple aliphatic or aromatic esters. Examples are amyl acetate, or banana oil, and methyl salicylate, or oil of wintergreen. But oil of turpentine and the oils of the citrus fruits consist largely of *cyclic hydrocarbons*—members of what is called the terpene series. Others, again, are largely aldehydes, ketones, or phenols, with smaller quantities of compounds containing sulfur or nitrogen.

The natural perfumes call for so much labor in collecting the blossoms from which they are obtained, and require such care during the process of extraction, that their price is necessarily very high. The organic chemist has accordingly entered this field, seeking first to identify the compounds responsible for the odor of the natural perfumes, and then to synthesize them from cheaper materials. Here the patient labor of the research chemists of two generations has at last won the same degree of success as in the synthesis of dyes and medicinal substances.

The artificial duplication of any of these odors involves, first, the separation of the natural material into its several constituents; second, the working out of the structural formula or plan of architecture of the molecules of the substances thus isolated; third, the synthesis of these substances from easily available raw material; fourth, the blending of the odoriferous substances thus produced to duplicate the natural perfume. The second and third steps are, of course, the most difficult and often call for years of expensive research. But even the final blending may prove a most vexatious problem, for many perfumes owe much of their distinctive odor to substances contained in them in traces too minute for identification.

Nevertheless, many natural flavors and perfumes have already had to yield much of the field to their synthetic duplicates. Essences of lilac and lily of the valley are now made in ton lots, from turpentine; essence of violet from lemon oil; vanilla from oil of cloves; and blends in imitation of the elusive odors of the rose and heliotrope, together with fragrant mixtures never known in nature, are produced in large quantities.

477. Synthetic Medicinal Substances

Among primitive peoples and in ancient times, the practice of medicine was in the hands of magicians and priests. With no scientific principles to guide them, they administered almost every imag-

inable substance as a medicine, very often with fatal results. But among countless failures, these early practitioners of the healing art now and then scored a success, discovering by pure accident some natural substance capable of exerting a well-marked physiological action or possessed of real curative properties.

Thus it was discovered that an extract of the bark of the cinchona tree, found in Peru, will cure malaria; that a preparation from the juice of the poppy induces sleep; and that certain plants produced poisonous substances which served as stimulants when administered in small doses. Various inorganic medicaments—preparations of arsenic, antimony, and mercury—were introduced during the Middle Ages. Within the last century came the discovery of general anesthesia by nitrous oxide, chloroform, or ether, and the use of numerous inorganic and organic substances as germicides and antiseptics.

We must, nevertheless, admit that medicinal substances found in nature have been employed very largely as they happen to occur, without any special attempts at purification. The chemical compounds responsible for their useful properties have often remained unknown; and the preparations that have been administered have been of uncertain strength and potency, and have often contained unknown amounts of ingredients of an actually harmful nature.

Moreover, such chemical substances as have been employed in medicine in a pure form were first prepared with quite other ends in view. Their physiological action was often brought to notice by merest chance, long after chemists had been familiar with their more obvious properties. Ether, for example, has been known since the thirteenth century, but its anesthetic properties were noted for the first time in 1846. Again, almost a quarter of a century elapsed after the discovery of amyl nitrite before it was found that this substance gave almost instant relief from the agonies of angina pectoris. Ethylene, hailed as a new anesthetic about 1924, was actually discovered in 1795.

There is no doubt that among the great host of synthetic organic compounds known today, perhaps 500,000 in number, are hundreds of which medicine might make use if their physiological properties were more fully known. Their investigation will engage the attention of many research workers during years to come. Synthetic chemists, too, will be active in producing compounds that are derived from or related to those produced by plants and animals, and in many instances are more effective than the natural product as curative agents.

New syntheses important in the field of medicine include anesthetics, vitamins, and the sulfa drugs. *Sulfadiazine* is made into an

ointment which is very effective for treating burns and skin infections. *Sulfaguanidine* is used in the tropics to combat dysentery. *Sulfathiazole* is taken internally and *sulfanilamide* is dusted into wounds. In this manner the loss of life from abdominal wounds has been reduced. In the recent war each American soldier's kit contained first aid doses of sulfanilamide, which may also be used for streptococcus infections. *Sulfapyridine* has been used in combatting pneumonia.

Military surgery has been aided by the timely synthesis of *pentothal*, which is injected intravenously to produce anesthesia.

Several thousand different substances have been synthesized and tested in the search for a cure for malaria. A few, including *atabrine*, administered alone or in conjunction with quinine, have shown great promise. Quinine itself has at last been synthesized, after nearly a century of effort.

An important new development is in the use of microorganisms to produce substances called *antibiotics*, which are inimical to other microorganisms. Thus they may often be used in the treatment of infectious diseases. Recent examples are *tyrothricin*, *penicillin*, and *streptomycin*. These and other antibiotics, still constantly being discovered, promise to be of value in combating many diseases, especially the viruses, for which no effective treatment is now known. Many of the new antibiotics will no doubt promptly be synthesized, and thus made available without the aid of the microorganisms that first produced them.

478. Hormones and Vitamins

Scattered through the body are a number of "ductless glands," so called because the chemical products that they secrete find no outlet for escape except by entering the blood stream. The secretions of these glands are substances called *hormones*, the minutest traces of which exert the most important influence on the vital activities. Growth-stimulating hormones see to it that we increase in size during childhood, then growth retarders step in and put an end to the process. Sex hormones are responsible for the infinite major and minor differences between the two sexes. The normal functioning of all the organs in the body appears to depend on traces of hormone chemical regulators that reach them in the blood stream.

We do not know how many hormones exist. There may possibly be dozens. A knowledge of their nature and functions and their production by synthesis would place us in complete control of a number of baffling diseases. During the past few years, about a dozen hormones have been isolated, and about four of them have been synthesized,

including thyroxine, an iodine compound secreted by the thyroid gland, and epinephrine (or adrenaline), which is secreted by the adrenal glands.

Investigators are also rapidly disclosing the chemical nature of the *vitamins*, which must be present in minute quantities in our food for normal health and growth. At present the control of derangements due to a lack of vitamins depends on the use of natural foodstuffs known to be rich in them. Synthesis of the vitamins has made rapid progress in recent years and eight or ten of them have now been produced in the laboratory.

Exercises

1. Write formulas for the three substances most commonly used for digesting wood chips in the manufacture of paper pulp. Write an ionic equation (§ 396, 397) to show why one of them, because of hydrolysis, reacts strongly alkaline when dissolved in water.

2. In which of the industries based on cellulose is this substance merely altered in form and in which is it converted into other substances?

3. What group or radical (§ 463) characterizes an alcohol? An aldehyde? An acid? An ester?

4. By counting atoms in the repeated unit of the cellulose chain molecule show that we may represent cellulose by the structural formula $(C_6H_{10}O_5)_n$, in which n represents the number of units in the chain.

5. If each repeated unit in the cellulose chain molecule is about 5×10^{-8} cm long, how many units compose a visible fiber 5 mm long?

6. Representing cellulose by a formula that will correctly show the number of hydroxyl groups in the repeated unit, write an equation to represent the reaction of cellulose with nitric acid to form a completely nitrated cellulose nitrate, with all the hydroxyl groups replaced by nitrate groups. The other product of this reaction is water. The sulfuric acid used in nitrating cellulose is to combine with and remove the water, thus rendering the reaction more nearly complete than it otherwise would be.

7. Write a graphic formula for trinitrotoluene (TNT), assuming that the 3 nitro groups replace 3 hydrogen atoms that are not in meta-positions (§ 462) with respect to the methyl group of toluene.

8. Which important cellulose plastics are esters and which are ethers?

9. Distinguish between thermoplastic and thermosetting resins. Mention several examples of each.

10. Casein and other proteins generally contain about 6.25 per cent nitrogen. What must be the average formula weight of the group R that occurs in the repeating unit of a protein chain molecule (§ 473)?

11. What is meant by polymerization? Co-polymerization?

12. With the aid of descriptions in the text and the table in § 472 suggest one or more plastic materials that might be used in each of the following applications:

Lacing for a tennis racket, fountain pen barrel, fish net, acid dipper, carburetor float, elastic belt, picture frame, fabric for covering a chemical laboratory manual,

adding machine keys, slide rule, circular illuminators for the dials of an airplane instrument board.

13. Nylon has been popularly described as being derived from coal, water, and air. Can you justify this, in view of the method of synthesis actually used?

14. What was Goodyear's discovery? What improvement did it effect in the properties of rubber?

15. What name is given the substance whose molecules become linked in forming a polymer?

16. What are some characteristics in which neoprene is superior to natural rubber?

17. Which of the various synthetic elastomers do you think suited in properties for the following uses: barrage balloons, gas masks, wrapping for replaceable parts for fine instruments, pneumatic lifebelts, hose for filling gasoline tanks, airhose for pneumatic drills, surface of a belt conveyor, interior of a belt conveyor, tire side walls, tire treads, collapsible boats.

Chapter 35

SILICON AND BORON

SILICON

479. A Comparison of Silicon with Carbon

Carbon and silicon each possess four valence electrons and manifest a covalence of four in almost all their compounds. Nevertheless there are important differences in the behavior of the two elements, owing to a difference in atomic radius:

1. Since silicon has a much larger atomic radius than carbon, its central positive charge attracts the outlying electrons less strongly. In the silicates, therefore, silicon tends to yield electrons to oxygen, thus leaving the silicon positively charged.

2. The striking difference between carbon and silicon is also manifested in the character of their oxides. The covalent compound CO_2 shows no tendency to polymerize (combine with itself), because in forming the covalent linkage of carbon to oxygen the valence electrons are all firmly held. In the linkage of silicon to oxygen, however, the weakened attraction of the silicon for electrons, because of its large diameter, makes possible the sharing of an oxygen atom between two different silicon atoms. The result is a crystalline solid, in which the atoms are all very firmly bound together. The crystalline silicates and quartz therefore possess high melting points, are non-volatile, and do not dissolve in any solvents except in a few that decompose them.

The simpler organic compounds, by contrast, are gaseous or volatile liquids. Even complicated organic compounds usually melt at fairly low temperatures and dissolve in a great variety of solvents—an indication that the crystalline lattice, in nearly every organic compound, is composed of neutral molecules, held together by weak forces.

3. Though carbon and silicon agree in forming compounds in which the covalence of the element is four, they differ in that carbon may coordinate (§ 252) at most four other atoms about it, whereas silicon

may coordinate six other atoms, as in the fluosilicates, which contain the fluosilicate ion, SiF_6^{--}.

The following table shows that silicon actually does form many covalent compounds, analogous to the corresponding carbon compounds, in spite of the important differences between the two elements that have just been emphasized:

CH_4	Methane	SiH_4	Silane
C_2H_6	Ethane	Si_2H_6	Disilane
C_3H_8	Propane	Si_3H_8	Trisilane
CH_3OH	Methanol	SiH_3OH	Silanol
$\begin{matrix}\mathrm{H}\diagdown \\ \mathrm{H}\diagup\end{matrix}\mathrm{C{=}O}$	Formaldehyde	$\begin{matrix}\mathrm{H}\diagdown \\ \mathrm{H}\diagup\end{matrix}\mathrm{Si{=}O}$	Oxosilane
$HCCl_3$	Chloroform	$HSiCl_3$	Trichlorosilane

Similarly for hundreds of other compounds. The structural formula of each of these silicon compounds is precisely like that of the analogous carbon compound; but stable compounds of silicon exist for which the corresponding compound of carbon appears to be incapable of existence.

In addition, there exist numerous compounds (the siloxanes) in which the group $-\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{H}}{\overset{|}{\underset{|}{\mathrm{Si}}}}}-\mathrm{O}-$ repeats in a chain or ring; also numerous compounds in which Si atoms replace a part of the carbon atoms of well-known organic compounds. Thus CH_3SiH_2OH, methyl silanol, is analogous to ethanol (ethyl alcohol), one of the two carbon atoms in the latter compound being replaced by silicon. This intermediate field between organic chemistry and the chemistry of the silane derivatives is growing at an astounding rate.[1]

480. Minerals

On the average, the earth's crust contains about two equivalents (§ 294) of metallic oxide for each formula weight of silica. In other words, the solid rocks have an average composition approximating salts of the hypothetical metasilicic acid, H_2SiO_3. But many individual rocks depart rather widely from this average. Rocks, for the most part, are not definite chemical compounds—though if they have cooled slowly enough they may contain crystals that are definite compounds,

[1] For the nomenclature of silicon compounds refer to *Chem. Eng. News*, **24,** 1233 (1946).

embedded in a glassy ground mass (supercooled liquid). Thus granite consists of three different types of crystals.

The chemical individuals that go to make up the igneous rocks (p. 330), derived from originally molten material by a process of crystallization, are called *primary minerals*. In addition, in the metamorphic rocks (p. 330) there are a great many derived or *secondary minerals*, produced by alteration of the primary minerals, through heat, pressure, or circulating water. Thus feldspar, the principal component of granite, may be altered to mica and quartz by heat and pressure, or may produce clay by weathering.

481. Classification of the Silicate Minerals

Silicate minerals are often classified according to their proportion of silica (SiO_2) in comparison with metallic oxides (CaO, MgO, Al_2O_3, etc.):

1. *Orthosilicates* are salts of the hypothetical orthosilicic acid, H_4SiO_4. Examples are Mg_2SiO_4 and Zn_2SiO_4.

2. *Metasilicates* are salts of the hypothetical metasilicic acid, H_2SiO_3. An example is $CaSiO_3$.

3. *Polysilicates* are minerals which are relatively richer in silica than the metasilicates. Included in this group are the *trisilicates*, salts of the hypothetical trisilicic acid, $H_4Si_3O_8$. Many but not all of the *feldspars* are trisilicates. They form the most abundant group of minerals in nature and make up about 60 per cent of the igneous rocks of the earth's crust. Potash feldspar (orthoclase), with the formula $KAlSi_3O_8$, forms the large, oblong, white or pinkish crystals that are conspicuous in ordinary granite.

The chemistry of the silicates is much more complicated and difficult than the broad classification just given may suggest. This is in part due to the fact that *cations with the same valence may often be substituted for one another in all possible proportions, in building a silicate crystal.* For example, an indefinite number of Ca^{++} ions, in the space lattice of a silicate mineral, may be replaced by Mg^{++}, Fe^{++}, or Mn^{++} ions. The result is a *solid solution*, which for a metasilicate would be formulated $(Ca, Mg, Fe, Mn)SiO_3$. The cations of elements within the parentheses are understood to be present in any desired proportions, subject only to the condition that the total positive charge which they contribute to the crystal shall be equal to the total negative charge due to metasilicate groups.

Moreover, *even elements of different valence may replace one another in the space lattice of a crystal, if they happen to possess nearly the same*

ionic radius. For example, it is now understood that Si^{+4} may be replaced by Al^{+3} or Be^{++}, without altering the fundamental structure of a silicate mineral, though the substitution of one of these ions for another will alter the total positive charge and must be compensated by an alteration in the total number of charges contributed by other groups or ions.

Whenever Al^{+3} or Be^{++} is substituted for Si^{+4} the classification of a mineral as an orthosilicate, metasilicate, etc., is misleading. These substitutions were late in being recognized; and it was only in 1928 that X-ray examination of silicate minerals, in the hands of a British

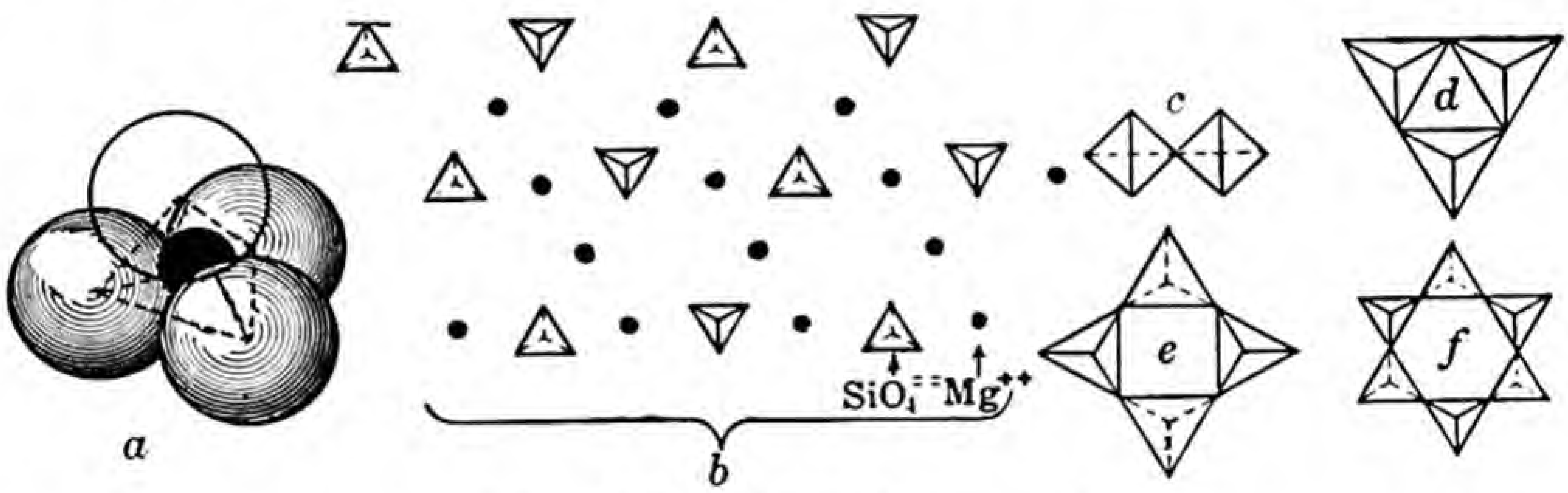


FIG. 148. Silicate structure.

physicist, W. L. Bragg, later extended by Pauling in the United States and by other workers elsewhere, revealed that the fundamental structural unit in silica and in all the crystalline silicates of whatever type is the $SiO_4^{==}$ group. The four oxygen ions, O^{--}, in this group occupy the four corners of a tetrahedron (triangular pyramid), with a silicon ion, Si^{+4}, in the center, as shown at *a* in Fig. 148.

In the orthosilicates, separate $SiO_4^{==}$ tetrahedra alternate in the space lattice with positively charged metallic ions, as shown in *b*, Fig. 148, which indicates the crystalline structure of the orthosilicate *olivine*. In some other classes of minerals the silicate tetrahedra are linked together in pairs, with an oxygen ion in common, as in *c;* or three, four, or six tetrahedra may share certain oxygen ions in common, to form rings (*d, e, f*). Still other structures are known, in which the tetrahedra are linked together to form chains, sheets, or a network in three dimensions.

482. Quartz and Other Forms of Silica

Silicon dioxide, SiO_2, is usually called *silica.* It is composed of silicate tetrahedra, linked together in a solid structure. Since each oxygen ion is shared between two different silicate tetrahedra, there are

only half as many oxygen ions in the completed solid structure as the formula $SiO_4^{==}$ would seem to suggest; in other words, the formula of the solid structure, extended indefinitely in three dimensions of space, is a triply infinite multiple of SiO_2. There are three different crystalline forms of silica, and each of these exists in two or more modifications, differing in physical properties, and doubtless representing different linkage patterns between each silicate tetrahedron and its neighbors.

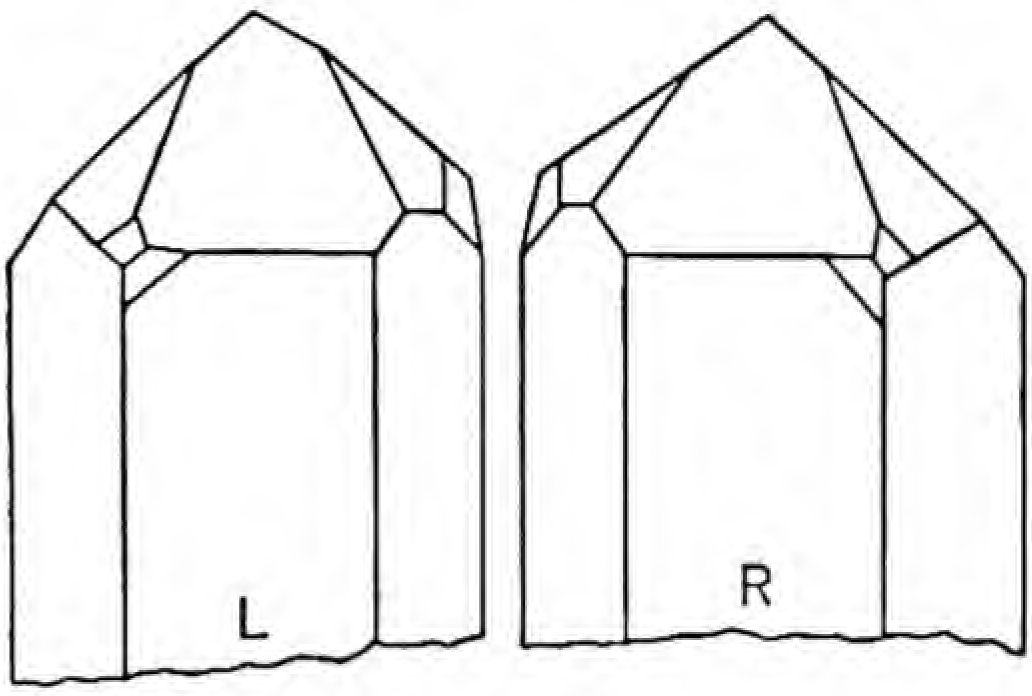


FIG. 149. The two types of quartz crystals here shown rotate the plane of plane-polarized light, respectively, to the left and right. Observe that the faces in each crystal are arranged in the opposite order to that of the corresponding faces in the other.

The most important crystalline form of silica is *quartz*. This is found in large transparent crystals, which are hard enough to scratch glass. As a mineral it is second only to the feldspars in abundance, and is estimated to compose about 12 per cent of all the igneous rocks of the earth.

Certain minute aquatic organisms (diatoms, infusoria) and certain varieties of sponges develop siliceous skeletons, which accumulate on the ocean bottom when the organisms die. Deposits up to a thousand feet in thickness have been found in various parts of the United States. This material is called *infusorial* or *diatomaceous earth* (*kieselguhr*). Mixed with a little soap and sodium carbonate it is used as a scouring powder (metal polishes), and it finds application for adsorbing and removing the coloring matter from edible oils. Flint is composed of sponge spicules or other siliceous organic residues, cemented together by colloidal silicic acid and hardened by slow dehydration under pressure.

Chemical apparatus of *fused silica*, made by fusing sand in an electric furnace, is now of importance in the laboratory as a substitute for platinum. By fusion in a vacuum furnace, bubbles of air are removed, and the product becomes transparent. Otherwise it is milky and opaque. Transparent fused silica has the advantage over glass of transmitting both visible and ultraviolet light.

Fused silica is cheaper than platinum, and less likely to lose weight on being heated strongly. It has a smaller coefficient of expansion than glass, and hence is less likely to crack on sudden cooling. Fused silica may be heated red hot and plunged into cold water without being injured. Its chief disadvantage is its gradual transformation, at

temperatures above 1100°C, into other crystalline varieties of silica, of inferior mechanical strength.

483. Hydrous Silica

When finely powdered silica is heated for a long time with water, best in an autoclave (§ 153) at temperatures above 100°C, a small part of it dissolves, forming a colloidal dispersion; the remainder absorbs 15 to 20 per cent of water, forming a transparent gelatinous mass or gel (§ 439), usually termed *hydrous silica.*

Hydrous silica is more readily prepared by treating a solution of a soluble silicate (water-glass, § 485) with an acid. There is obtained a highly hydrous, gelatinous form of silica, which loses water gradually and continuously if squeezed in a press, or even if exposed to a dry atmosphere. Eventually but a few per cent of water may remain. Thus we know all possible stages between completely anhydrous silica and gels containing as much as 98 per cent of water. There is no evidence of the formation of a definite hydrate of silica, of invariable composition.

Silica gel is made by treating a warm solution of water-glass with an acid, washing the precipitate of gelatinous hydrous silica with hot water, drying it at room temperature, then in an oven for a few hours, gradually raising the temperature from 75° to 120°. Final drying may be at 300°C for perhaps half an hour. It is used for adsorbing gasoline from natural gas, and sometimes as an adsorbent in household refrigerating systems operated by gas flames. It is a useful carrier for platinum black (finely divided metallic platinum), used as a catalyst in many reactions.

484. Some Industrially Important Silicates

Asbestos owes its fibrous structure to the linking of silicate groups in continuous chains. The most important varieties of asbestos are *hydrated magnesium silicates.* The *amphibole* or double-chain variety has the advantage of being acid-resistant and more infusible at high temperatures. It is accordingly used for packing steam pipes and furnaces, and in the chemical industries for filtering acid. The longer-fibered, less heat-resistant variety (*chrysotile*), coming chiefly from eastern Canada, is woven into fireproof fabrics.

Closely related to asbestos is *talc*, also a hydrated magnesium silicate. This is a white mineral, with a flaky texture. It is soft enough to be scratched with the finger nail, and so smooth as to be almost greasy to the touch. It is used in cosmetics, for filling writing paper, for finishing leather, and for polishing glass and metals.

Mica is a familiar transparent mineral, chiefly used in electrical condensers. This is *muscovite*, or potash mica, a hydrated potassium-aluminum silicate. X-ray examination shows why mica splits so readily along parallel planes. The $SiO_4^{==}$ groups are linked to each other in two dimensions to form flat sheets, each separated from the next by a layer of cations. The limit of thinness of sheet mica is that of the individual silicate sheets, which is roughly 2.5×10^{-8} cm, or a hundred-millionth part of an inch. Mica has nearly the same hardness as metallic copper and is therefore useful as an insulator between the commutator bars of dynamo electric machinery. Its use in condensers has tended to decrease during recent years.

The *zeolites* are a group of hydrated sodium-calcium alumino-silicates, of widely variable composition, occurring in many weathered rocks and soils. They are remarkable in that their sodium is readily replaced by other cations and that the quantity of water they contain is continuously variable within wide limits, without disrupting the crystal structure. This is in striking contrast with the collapse of the crystal structure that is produced whenever water of hydration, incorporated in a crystal lattice, is expelled by heating. In brief, *the water of zeolites is loosely held in some other manner than as a part of the crystal lattice, and cations within the crystal are readily replaceable by other cations.*

X-ray examination of the zeolites has yielded a clue to their mysterious behavior. As many as half the silicon atoms of the $SiO_4^{==}$ groups are replaced in the zeolite by aluminum atoms, in an open structure, somewhat resembling a honeycomb. This replacement of Si^{+4} by Al^{+3} leaves the network with a negative charge. The extra cations that are needed to produce electrical neutrality are then fitted into the vacant spaces in the network. This explains why sodium ions in the interior of what appears to be a solid crystal are nevertheless subject to replacement by other cations, and why the quantity of water in the crystal may vary within wide limits.

485. Water-Glass

By heating sodium carbonate or potassium carbonate at a bright red heat with finely powdered silica a readily fusible silicate is obtained, usually containing $x = 1.7$ to 3.9 molecules of silica for each molecule of sodium or potassium oxide:

$$Na_2CO_3 + xSiO_2 \rightarrow \underset{\text{Sodium silicate}}{Na_2O \cdot xSiO_2} + CO_2 \uparrow$$

The molten product thus obtained solidifies upon cooling, forming a glassy solid. If it is poured into cold water while still in the molten condition it is dispersed to form a viscous colloidal dispersion, moderately alkaline toward indicators. This is *water-glass*.

Water-glass solution is used (1) for water-proofing stone surfaces; (2) as an adhesive in making pasteboard boxes; (3) to *deflocculate* water-clay mixtures, in casting pottery; (4) as an adhesive for abrasive materials, in grinding-wheels; (5) as a water softener, either alone, or as a component of laundry soap; (6) as a cleansing and weighting agent in the textile industries; (7) as a paint remover (owing to its alkalinity). (8) Eggs may be preserved for a long time by being submerged in a water-glass solution of moderate concentration (density about 1.05). Vats to contain dilute acids are often lined with tile set in a paste of powdered talc and water-glass.

Sodium metasilicate is now marketed as readily soluble crystals.

486. Lime-Soda Glass

Any mineral substance which breaks with a characteristic glassy fracture, and possesses a vitreous or glassy luster, with some degree of transparency, is often referred to loosely as a glass. Ordinary soft glass, or *lime-soda glass*, used for window panes and bottles, is a sodium-calcium silicate; but useful glasses have been prepared containing none of the three elements Na, Ca, Si.

Courtesy of Pittsburgh Plate Glass Co.

FIG. 150. Pouring molten glass, to be rolled into sheets.

The most important raw materials for the manufacture of common glass are calcium carbonate, sodium carbonate, and quartz. These must be very finely powdered and intimately mixed. If the glass is to be colorless the raw material should be free from more than traces of iron. When such a mixture is heated in a furnace the silica reacts with carbonates, expelling carbon dioxide. After a few hours the contents of the crucible melt into a clear liquid, which is purified

by skimming, then cast or blown into molds, or is rolled into sheets (Fig. 150), which are afterward polished (plate glass).

Sodium sulfate, in the presence of powdered coke, which serves as a reducing agent, is often substituted for sodium carbonate in the manufacture of glass. The best lime-soda glasses approximate the formula $Na_2O \cdot CaO \cdot 6$ to $8\ SiO_2$.

Colored glass is made by the addition of oxides of the heavy metals, to form colored silicates. Cobalt oxide gives a blue color; selenium dioxide or gold oxide, a ruby-red; cupric oxide, a blue under oxidizing conditions, or a dull red (metallic copper) under reducing conditions; chromic oxide, a green; silver oxide, a yellow; manganese dioxide, a violet.

487. Optical and Chemical Glassware

Glass which is to be used for lenses must be almost colorless, and uncommonly free from defects due to enclosed air bubbles, solid particles, or lack of uniform composition. These requirements mean that optical glass must be stirred for a long time in the melting-pot, and cooled very slowly during a period of days, weeks, or months.

The older optical glasses were classed as *crown* (lime-soda-potash) and *flint* (lead oxide-soda-potash) glass. By a combination of these two kinds of glasses it is possible to produce a lens that will form an image that is both *anastigmatic* (free from distortion) and *achromatic* (free from rings of color). In the modern optical glasses a part or all of the silica is often replaced by boric oxide (B_2O_3) or phosphoric oxide (P_2O_5); and a part or all of the lime and soda by the oxides of barium, zinc, magnesium, or even aluminum.

Chemical laboratory apparatus needs to be (1) mechanically strong; (2) less likely to break than ordinary glass when subjected to sudden temperature changes; and (3) as nearly insoluble as possible in water, dilute acids, or dilute alkalies. Increased resistance to mechanical and thermal shocks is obtained by substituting B_2O_3 for a part of the SiO_2 of common soft glass; and decreased solubility by replacing most of the alkalies (Na_2O and K_2O) and lime (CaO) by Al_2O_3, ZnO, or even Sb_2O_3. "Pyrex" glass is a well-known borosilicate glass of American manufacture, possessing great resistance to chemical reagents or sudden temperature changes.

A remarkable glass has recently been prepared by leaching out most of the non-siliceous components of a special high-silica glass, leaving a network of nearly pure silica, which may be fused to form a completely transparent glass that is extremely resistant not only to mechanical shock but also to sudden changes in temperature. When

this process has been commercialized we may expect to see glass baking dishes even superior to the remarkably shock-resistant borosilicate (Pyrex) glass dishes now in common use.

It has recently been found that glass heated almost to the softening temperature, then suddenly cooled with a blast of cold air, may acquire a tough surface film that enables it to withstand mechanical shocks. Chemical glassware thus treated may be dropped from a table to a concrete floor without being shattered.

488. Fiber Glass

Although fibers of spun glass have been known for several centuries it is only within the last few years that this material has been produced with sufficient flexibility and other properties to enable it to be woven into fabrics. Its principal use is in woven tapes for wrapping the armatures of electric dynamos and motors. The wrapped armatures are dipped in a Bakelite (phenolic resin) lacquer (§ 468) and heated to a sufficiently high temperature to set the varnish permanently, thus giving a coating that has excellent electrical resistance, is impervious to moisture, and is capable of withstanding high temperatures indefinitely, without deterioration. Considerable reduction in the size and weight of motors is thus obtained, since they may safely operate at much higher temperatures when insulated by fiber glass instead of cotton, silk, or oil-impregnated paper.

Glass fiber is very useful as a heat insulator within the walls of buildings, and textile fabrics woven from the same material are beginning to appear as window drapes, door hangings, and table covers. These will doubtless presently be produced in colored patterns, through the development of processes for color printing the woven glass textiles.

Boron

489. Boron and Boron Minerals

From the position of boron, at the head of column 3A in the periodic table, we should expect it to be related to aluminum. Both elements do in fact possess 3 valence electrons, and manifest a covalence of 3 in many compounds. Nevertheless, boron is definitely *non-metallic* and more closely related to silicon than to any other element. This is because the small radius of the boron atom makes it tend to form covalent bonds with neighboring atoms. Boron trioxide replaces silicon dioxide in many glasses, glazes, and enamels. This replacement, in spite of a difference in valence, is made possible by the fact that B^{+3} (in B_2O_3) and Si^{+4} (in SiO_2) are of nearly the same size.

Elementary boron is prepared by reduction of the oxide, B_2O_3, in a covered crucible, with a limited amount of metallic sodium, potassium, magnesium, or aluminum. Boron occurs in traces in a great many igneous rocks. The workable deposits of boron minerals occur mainly in dry countries, the most important ones in the United States being *borax*, or sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$; and *colemanite*, a calcium borate, $Ca_2B_6O_{11} \cdot 5H_2O$. These occur in almost inexhaustible quantities in the alkaline lakes and deserts of Nevada and southern California.

490. Boric Acids and Borates

When a warm solution of borax is treated with a dilute acid, a precipitate of boric acid [2] (orthoboric acid), H_3BO_3, is produced. This is a slightly soluble substance that separates in glistening white flakes as the solution cools. It is somewhat volatile with steam, a fact that accounts for its presence in jets of water vapor that issue from the ground in the neighborhood of certain volcanoes. It is used in medicine, in antiseptic solutions.

If orthoboric acid is heated in the air, it loses water, forming metaboric acid, HBO_2, then tetraboric acid, $H_2B_4O_7$, and finally boron trioxide, B_2O_3. These all revert to orthoboric acid when dissolved in water.

Borates (salts of the preceding acids) are nearly completely hydrolyzed (§ 396), hence react strongly alkaline, when dissolved in water. With borax, for example, the reaction is

$$B_4O_7^{--} + 7HOH \rightleftharpoons 4H_3BO_3 + 2OH^-$$

The alkaline reaction of borax solutions makes borax useful as an ingredient of washing powders. Borax is also used for softening water, since calcium and magnesium borates are insoluble. Other uses are as a flux in soldering, and in the preparation of enamels and heat-resistant glasses.

TECHNICAL WORDS

Rock, p. 563. **Mineral,** p. 19. **Ore,** p. 19.
Primary mineral, p. 564. **Secondary mineral,** p. 564.
Hydrous, p. 168. **Gel,** p. 505.
Deflocculate—to disperse suspended particles to colloidal or nearly colloidal dimensions.
Anastigmatic, achromatic (terms referring to lenses), p. 570.
Enamel—a glassy coating, usually opaque, capable of adhering tightly to the surface of a metal, glass, or ceramic product.

[2] Also called *boracic* acid, particularly in medicine.

Chapter 36

THE METALS

491. Physical Properties of Metals

The outward forms of our civilization, our manner of living, and hence our manner of thinking, are greatly influenced by the uses that we make of metals. We entrust our lives to their *tensile strength*, in the steel frameworks of buildings, the wrought iron or mild steel cables of elevators and bridges, the light-metal trusses of airplane structures. Their *electrical conductivity* enables energy to be transported long distances to light cities, propel trains, and drive the motors of a thousand industries, meanwhile giving us instant communication without regard to distance, and filling all the world with noise and propaganda.

The *thermal conductivity* of metals is put to use in steam engineering, in heating or refrigeration systems, and in cooling internal-combustion engines, thus making possible the automobile and airplane. Their *malleability* and *ductility* enable us very cheaply to fashion them into the multitude of forms that their multitude of uses demand. Their *metallic luster* lends beauty to objects that otherwise would merely have strength, and by mirroring the external forms of things enables us to dress for dinner or photograph the spiral nebulae.

492. Accounting for the Physical Properties of Metals

We can account in a large measure for the physical properties of metals by the simple fact that *metallic atoms are relatively poor in valence electrons*. Most of them have only one or two electrons in the outermost shell or highest energy level. Yet most of them, in metallic crystals, make contact with either eight or twelve neighboring atoms.[1] There are obviously not enough valence electrons to establish covalent bonds between each metallic atom and all its neighbors. So the atoms

[1] The only exceptions are manganese and about 6 or 8 metals and semi-metals in columns, 3A to 6A, toward the right-hand lower corner of the periodic table.

in a typical metallic crystal are not rigidly linked together, with bonds that are definitely oriented in space, but instead possess a mobile linkage, with valence forces diffused evenly in all directions. (Ex. 1.)

The mobile linkage of the atoms in a typical metal permit them to roll over or slip past one another along definite *slip planes*, almost as if they were rigid spheres. Thus we account for the *malleability* and *ductility* of metals. The metals that are least malleable or ductile are the very ones whose atoms possess more than two electrons in the outermost shell or highest energy level.

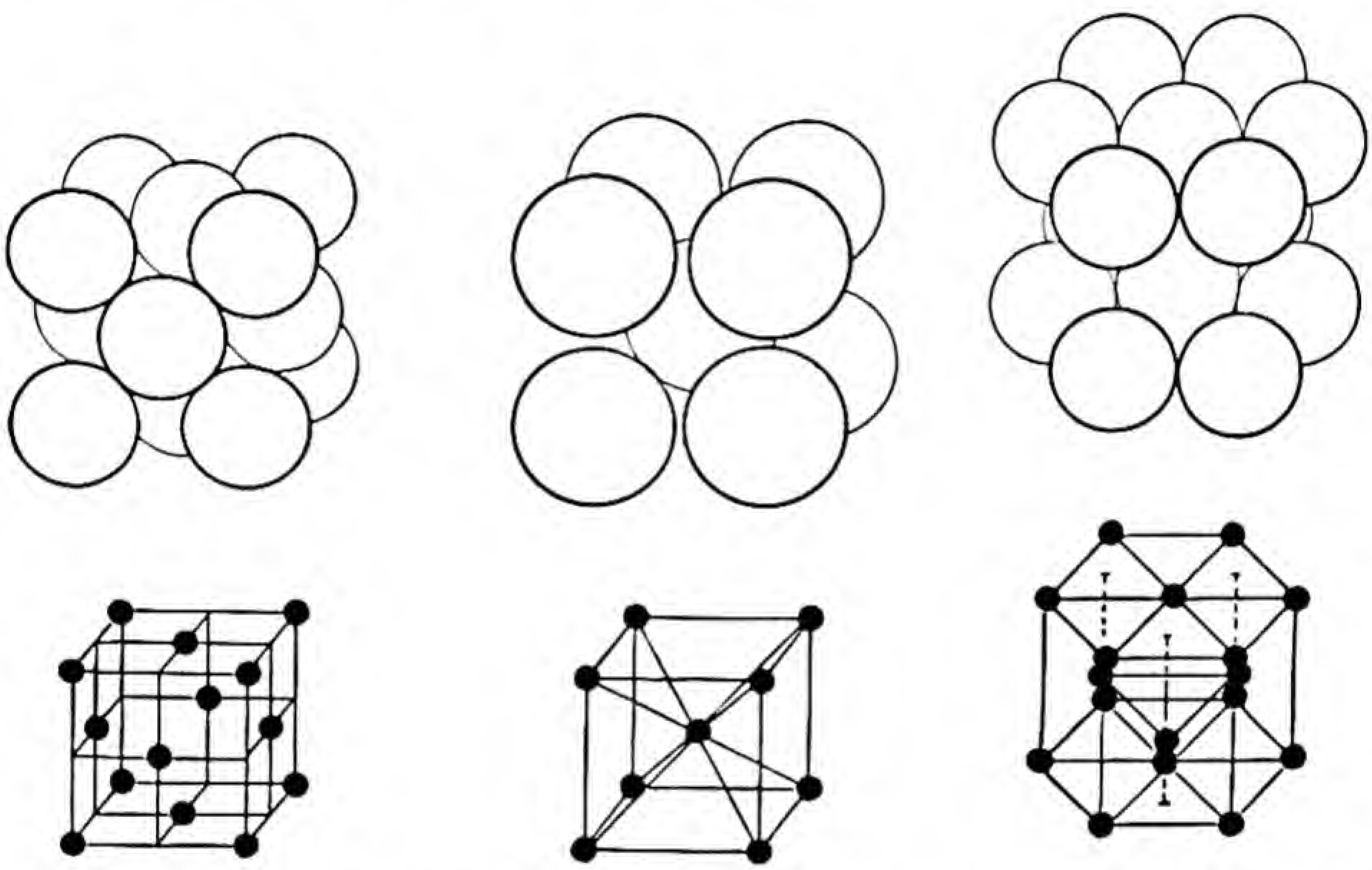


Fig. 151. Three types of close-packing of atoms within crystals. In the face-centered cubic packing, shown on the left, and in the hexagonal close-packed arrangement, shown on the right, each atom has twelve nearest neighbors. In the body-centered cubic packing, shown in the center, each atom has eight nearest neighbors.

The fact that metals are good conductors of heat and electricity leads us to believe that a certain proportion of the valence electrons possessed by metallic atoms are somewhat mobile, in other words, may pass freely from one atom to another. *An electric current through a metal* consists of a stream of these mobile electrons, flowing among and between the atoms, from the terminal of the metallic circuit that has a surplus of electrons (the negative terminal) to the one that has a deficiency of electrons (the positive terminal). (Ex. 2.)

A flow of heat through a metal consists of the transfer of disordered motion, possessed by the atomic nuclei at the hot end of the metal, thence handed on to the mobile electrons, which in turn rouse more distant nuclei. For this reason conductivity for electricity and con-

ductivity for heat tend to rise and fall together, as we compare one element with another.

Metallic luster seems accounted for by assuming that the mobile electrons within metals may be set in motion by light quanta (photons) of all the visible frequencies, momentarily accepting their energy, but immediately reemitting it. Because light quanta are thus intercepted and extinguished by the mobile electrons we find that all metals, except in layers only a few atoms thick, are non-transparent. A transparent material is one with its electrons bound fast, and, so far as we know, is always a very poor conductor of heat and electricity.

493. Zones of Electrons around Metallic Nuclei

The picture just presented of the internal structure of metals still leaves some details to be filled in. Metals have an atomic heat capacity (§ 146) of about 6 calories at room temperature, the same as non-metals (Law of Dulong and Petit). This fact convinces us that no very large proportion of the electrons in metals are mobile. If they were they would be roused into more and more energetic motion as the temperature is raised, as if they were independent extra atoms. Such a material would absorb at least twice the quantity of heat, in being heated through any chosen temperature range, that metals are actually observed to do. (Ex. 3.)

So we conclude that most of the electrons in a metallic crystal, even most of the valence electrons, are not free to migrate from atom to atom, but have limits set to their wanderings, each electron remaining under the control of a particular nucleus. This is the same as saying that the atoms that compose a metal are to be considered as uncharged atoms, rather than as ions, in spite of the fact that a small proportion of the electrons may leave one atom and pass over to another. It follows that the bonds between atoms in a typical metal are more like covalent bonds than they are like the electrostatic forces holding ions together. They are really covalent bonds that have lost their definitely directed character, and have become diffused and nearly equally directed in all directions about any given atom. (Ex. 4.)

Recent workers, guided by wave mechanics (§ 236), think of the nucleus of every atom in a metallic crystal as being surrounded by a series of concentric zones, each representing some definite potential energy. The outermost zones are occupied only by electrons that have been lifted to a higher energy level by energy acquired from the vibrating nuclei. If the arrangement of electrons within an atom and

the distances between atoms happen to be favorable the outermost zones or zones of highest potential energy, around neighboring nuclei, may overlap, as at A, A, Fig. 152. Electrons whose energy places them in the overlapping regions belong to no particular atom and are classed as mobile. The rest, in fact the great majority of the electrons, are mere satellites about particular nuclei, as they are in the isolated atoms of a metallic vapor.

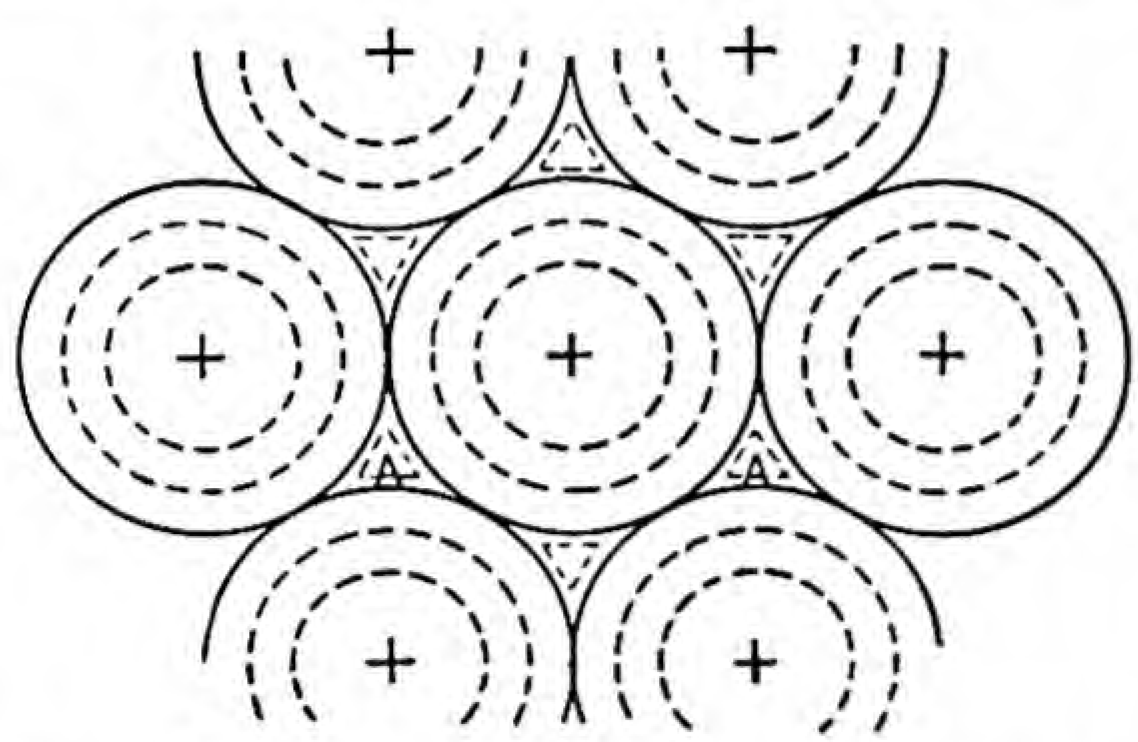


FIG. 152. Zones of potential energy around the nuclei of metallic atoms.

By altering the distribution of electrons within an atom (as in transferring an electron from the outer shell to an incomplete inner shell of a transition metal, § 544), or by altering the distance between atoms, the overlapping of zones may be altered. That is why different allotropic forms of a metal differ in conductivity. Or the zones representing the highest energy level in neighboring atoms may fail to overlap at all. That is why different elements or their allotropic forms may be classified sharply as conductors, like graphite, or complete non-conductors, like diamond.

The dissipation of energy as heat, when an electric current flows through a metallic conductor, is proof that the mobile electrons (at least in an imperfect crystal, or in the presence of impurities) may transfer their energy to the nuclei of atoms. The vibration of these, in random directions, we recognize as heat.

With increasing temperature the nuclei vibrate through wider and wider arcs, hence more frequently collide with the streaming mobile electrons. Most metals therefore show increasing electrical resistance, with increasing temperature.[2] If the temperature is greatly lowered the resistance decreases very rapidly; indeed a few metals (lead, mercury, tin, etc.), at temperatures within about 4 degrees of absolute zero, become practically perfect electrical conductors, for reasons not yet well understood. None of the best conductors (Ag, Cu, Au, Al, alkali metals) shows this low-temperature *superconductivity*.

[2] A few metals apparently possess electrons that are used in establishing covalent bonds between neighboring atoms. As the temperature rises these electrons tend to become freed. The resistance of such a metal passes through a minimum at some temperature.

494. Tensile Strength and Melting Point

One might guess that metals with the largest proportion of mobile electrons would not only be the best thermal and electrical conductors but would also possess weak bonds between atoms and hence *low tensile strength* and *low melting points*. In general, this seems true. The best electrical conductors, rated by atomic conductivity,[3] are the soft, weak, easily melted alkali metals, and the univalent heavy metals (Cu, Ag, Au). For other common metals a rough parallelism between tensile strength and melting point is shown in the accompanying table, in which the metals are arranged in the order of *decreasing melting point*, which turns out to be very nearly the order of *decreasing tensile strength.*

Aluminum is unusual for a metal with three valence electrons. Its high electrical conductivity, low tensile strength, and moderate melting point make it seem to resemble gold and silver, which possess only one electron in the highest energy level. It seems likely that the atoms in a metallic crystal do not always have the distribution of electrons assigned them in the Periodic Table facing the back cover. The table is chiefly based on spectral data, and shows the distribution of the electrons at high temperatures in atoms that are far removed from any neighbors.

A COMPARISON OF A FEW STRONG AND WEAK METALS

	Melting Point, °C	*Atomic Conductivity* (20°C)	*Tensile Strength, Lb per Sq In.*
Tungsten, drawn	3400	1.7×10^6	590,000
Iron, hard drawn	1530	0.7×10^6	80,000–100,000
Nickel, drawn	1452	0.87×10^6	155,000
Copper, wire	1080	4.0×10^6	60,000–70,000
Gold, wire	1063	4.2×10^6	20,000
Silver, wire	960	6.9×10^6	42,000
Aluminum, wire	658	3.5×10^6	30,000–100,000
Magnesium, drawn	651	3.0×10^6	33,000
Lead, drawn	327	0.86×10^6	2,600–3,300
Tin, drawn	232	1.4×10^6	4,000–5,000
Sodium	97.5	5.1×10^6	....
Mercury (solid) (−40°C)	−40	0.6×10^6	Very slight

[3] The conductivity of a gram atom of a metal, in *mhos* (p. 615) measured between parallel electrodes 1 cm apart.

495. Alloys

By intermingling or combining metals with one another we obtain *alloys*, with the most astounding range of properties. We know alloys that are really solid, yet so soft that they yield perceptibly to the stroke of a feather. We have others so hard that they cut the hardest steel and will almost scratch diamonds. We have tungsten alloys, with nearly twice the density of iron, and others containing beryllium or magnesium that are lighter and tougher than aluminum.

We have low-melting alloys for electric fuses; acid-resisting alloys, such as stainless steel and stellite; alloys that catch fire with slight friction or even on being exposed to the air; alloys that will withstand a bright white heat in contact with air or steam, without being tarnished. There are alloys of very high electrical conductivity, and others distinguished by high resistance.

Some alloys are revealed as homogeneous, when examined with a microscope; others consist of extremely hard particles imbedded in a plastic matrix; and others still show patterns of interlocking crystals of several distinct types. Some alloys are hardly more permeable to magnetism than wood or air, whereas others may be magnetized far more intensely than soft iron. To such developments in the field of synthetic metals our generation owes high-speed trains, the long-distance telephone, household refrigerators, more efficient incandescent lights, improved radio tubes, corrosion-resistant fixtures in the home and office, the thrills of aviation, and the possibility of being wiped out in air raids.

Alloys may be prepared (1) by joint electrodeposition of two or more metals (§ 522) or (2) by adding or withdrawing certain components to or from other alloys. More commonly, they are made (3) by melting the predominating component or the one that is more easily melted, then dissolving the other component in it, with precautions to prevent oxidation.

496. Three Classes of Alloys

Let us prepare an alloy, remove and polish a specimen, and examine it under the microscope. We discover that it belongs to any one of three classes, or a combination of two or three of them:

1. *Components not miscible in the solid state* (though perhaps partially or completely miscible when melted). The solid alloy, under the microscope, will then present a mottled appearance, certain areas being pure component A, others pure component B, etc.

2. *Components intermingle in the solid state to form a solid solution*

with a composition that may be varied continuously, within certain limits (or occasionally, without limit), just as with a liquid solution. The solid solution will be represented by certain areas in the microscopic pattern, and any undissolved surplus of either component will separate in other areas (Fig. 153).

3. *Components intermingle or combine in the solid state* to form an *intermediate phase*—one whose *composition* is intermediate between those of saturated solid solutions of the two components in each

FIG. 153. Photomicrographs of alloy specimens that have been polished and etched. The left-hand figure shows white cast iron, etched with alcoholic nitric acid. Observe white areas, *A*, of cementite, Fe_3C, with dark areas, *B*, of graphite. The right-hand figure shows an alloy, 70% Cu, 30% Ni, etched with a mixture of nitric and chromic acids.

other, and whose *crystalline structure* is distinct from either. An intermediate phase is usually of somewhat variable composition, though it may approximate that represented by some definite chemical formula.

If the components entering into an alloy are intermingled in just the right proportions to form a definite intermediate phase, the microscopic field will usually show a mosaic of interlocking grains, all of the same composition. Impurities tend to collect in a film of apparently amorphous material, between the grains. An excess of any component beyond that demanded to form the intermediate phase may separate, nearly pure, or may form areas of a different intermediate phase.

497. Accounting for the Different Types of Alloys

We have just encountered an astonishing fact. Briefly stated, many metals, in the solid state, are *completely immiscible* with one

another; others intermingle within limited proportions or even in all proportions, forming *solid solutions;* others still combine or intermingle to form *intermediate phases.* But why? And why do intermediate phases of nearly definite composition often have such bizarre formulas as Cu_5Zn_8, or Cu_9Al_4, or $Cu_7Zn_4Al_2$, seemingly in entire disregard of all the rules of valence?

We are still far from knowing complete answers to questions such as these, for there are over 3000 possible pairs among the nearly 80 metals and semi-metals, and for each of these pairs all achievable proportions need to be investigated. The number of possible alloys containing more than two component metals is nearly limitless. Whichever way we turn, accumulated data seem woefully incomplete.

A few general principles have nevertheless been recognized, in spite of the handicap of incomplete information. It turns out that the controlling factors, in determining the structure of an alloy, are frequently *atomic radius* and the *electron-atom ratio*, defined as

(*Total number of valence electrons*) ÷ (*Total number of atoms*)

For example:

1. Metals having nearly the same atomic radius (differing by not more than about 10 to 12 per cent) will usually dissolve in each other to form solid solutions, and if they are *small* and have *the same number of valence electrons* they will usually be miscible in all proportions.

2. Metals whose atoms are of very different sizes are usually nearly immiscible in the solid state, whenever they have the same valence; but if they differ in valence by two or more units they will tend to form intermediate phases, or even definite compounds.

3. The solubility of one solid metal in another, the intermediate phases formed, and the type of crystal structure obtained are often determined by the electron-atom ratio. For example, when solid copper or silver is the solvent, another metal of favorable atomic radius may dissolve in the copper until the electron-atom ratio is about 1.4. Thus, when copper dissolves zinc to form α-brass, the saturated solid solution contains 61.6 atoms of copper (1 valence electron each) for every 38.4 atoms of zinc (2 valence electrons each). The electron-atom ratio is then

$$\frac{(61.6 \times 1) + (38.4 \times 2)}{100} = 1.384$$

But with copper (1 valence electron) and aluminum (3 valence electrons) this ratio is reached when only 20 atoms of aluminum are

present in every 100; with copper and silicon (4 valence electrons) it is reached with only 14 atoms of silicon in every 100. Tin has the same number of valence electrons as silicon, but is less soluble than silicon in solid copper, because its atoms are of an unfavorable size. *In calculating the electron-atom ratio, metals of the transition triads* (Fe, Pt, etc., § 212) *are ordinarily considered, somewhat arbitrarily, as having zero valence electrons.* (Ex. 5, 6.)

Figure 154 shows what sorts of alloys are actually formed between each metal and its nearest neighbors in the Periodic Table. The reader may easily convince himself that the rules we have given really

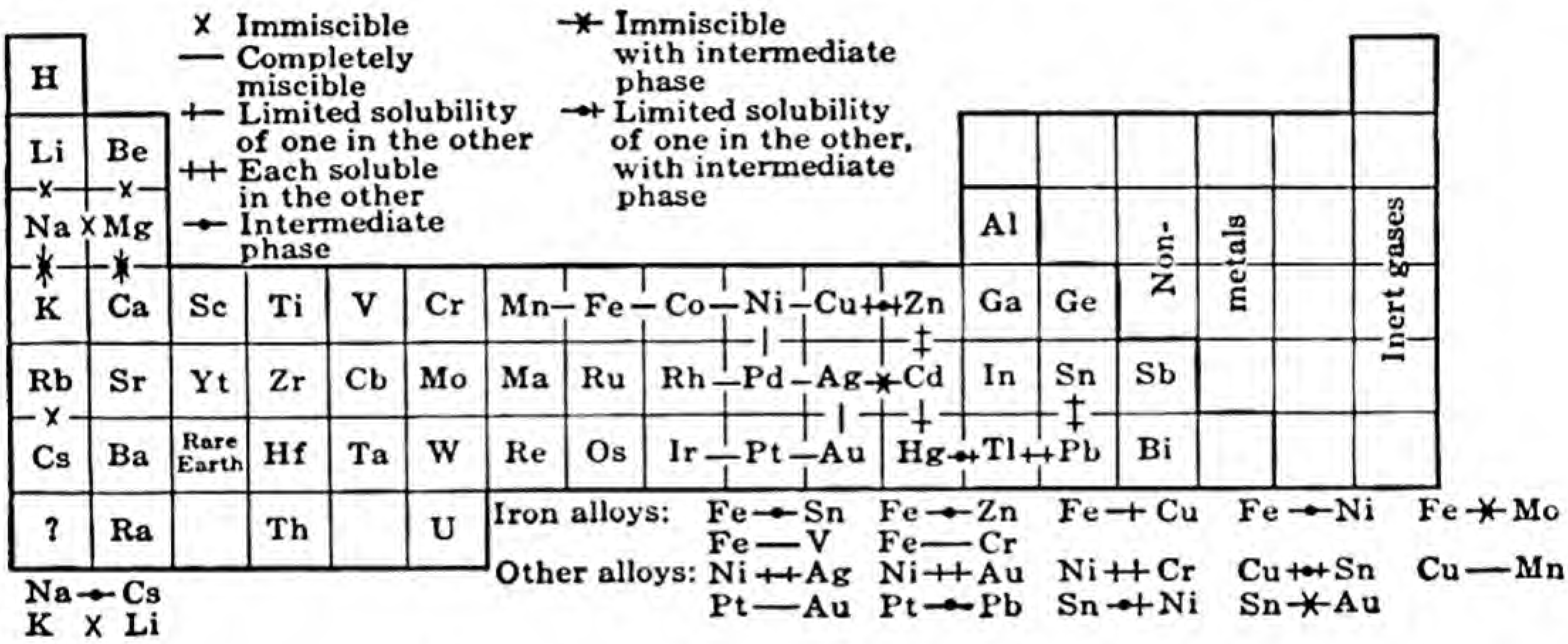


FIG. 154. Alloys and the Periodic Table.

hold in most instances. *Metals that are widely separated in the table are likely to form intermediate phases, perhaps including definite compounds; if very different in atomic radius they may form interstitial compounds, discussed in* § 499.

498. Intermediate Phases in Alloys

Intermediate phases in alloys are often referred to as *intermetallic compounds*, though they differ from ordinary ionic or molecular compounds in being somewhat variable in composition. A fine example is furnished by three different types of brass, which are intermediate in composition between the solid solution of zinc in copper already mentioned (α-brass) and a solid solution of copper in zinc (η-brass):

		Approximate Formula	*Electron-Atom Ratio*
α-Brass		(solid solution)	<3:2
β-Brass	Intermediate phases	CuZn	3:2
γ-Brass	Intermediate phases	Cu_5Zn_8	21:13
ϵ-Brass	Intermediate phases	$CuZn_3$	7:4
η-Brass		(solid solution)	>7:4

Alloys of other metals than copper and zinc often have the same crystal structure as the different brasses, provided that they possess the same electron-atom ratio. Thus Cu_9Al_4, Ag_5Cd_8, $Cu_{31}Sn_8$, and Ni_5Zn_{21} (in which Ni is assumed zero-valent) have the same electron-atom ratio and the same crystal structure as γ-brass, Cu_5Zn_8. (Ex. 7.)

The properties of brass, of course, vary with its structure. The α and β types, especially the former, are strong and ductile, but the γ and ϵ types are so brittle and hard they are nearly useless. The conductivity of β-brass is almost equal to that of pure copper, but the other varieties are much poorer conductors. *Solid solutions are probably always worse conductors than their pure components.*

If we ask why intermediate phases, among metallic alloys, should be of variable composition the answer is that there is really no reason for their being otherwise. *Ionic compounds* are of invariable composition because cations and anions must ordinarily be present in some definite proportion, in order that the material may be electrically neutral.[4] *Molecular compounds* are of invariable composition because definite numbers of atoms are linked by covalent bonds, in forming every molecule. But within a *solid alloy* the valence forces are neither ionic nor covalent, but the diffuse, undirected forces characteristic of the metallic state. So there are no very definite ratios between the numbers of the different sorts of atoms forming the alloy. Instead, the crystal structure, in many instances, is determined by the fact that every unit cell (§ 141) must contain a definite total number of atoms, reasonably uniform in size, with a total number of valence electrons that cannot exceed a fairly definite upper limit without making the whole structure unstable.

499. Solid Solutions versus Interstitial Compounds

In forming a solid solution, different sorts of atoms of approximately the same size usually take up *random positions* in the space lattice. In α-brass, for example, atoms of zinc replace random atoms of copper in the crystal lattice of pure copper. Nevertheless, when the different sorts of atoms are present in a solid solution in some simple ratio they are sometimes rearranged within the lattice, at some fairly definite "critical temperature," to give a regular alternation of atoms, often called a *superstructure.* Fountain-pen points, of gold alloyed with copper, are frequently thus hardened.

[4] We have seen that even this requirement does not prevent certain types of silicates (§ 481) from being of variable composition.

Whether an ordered superstructure is formed or an unordered solid solution, the limit of solubility of one metal in another is likely to be determined by the maximum permissible electron-atom ratio. *It is only when two lattices are of the same type and the interatomic distances are nearly equal that one sort of atom may replace another in all proportions.* Alloys of copper and gold or of silver and gold are an example.

In contrast with ordinary solid solutions, just described, are the *interstitial solutions*, often called *interstitial compounds*, in which atoms of a *metal* determine the crystal structure, but small atoms of a *non-metal* penetrate into the spaces between the metallic atoms, perhaps straining and distorting the crystal structure to some extent. Thus we account for hydrides, borides, carbides, and nitrides of the heavy metals, particularly of the transition triads (Fe, Ni, Co; Os, Ir, Pt; etc.). The penetrating atoms (of H, B, C, or N) must have a diameter less than about 0.6 of that of the atoms forming the primary lattice. The former often penetrate between the latter until the interstices are all full. The final product will then have a definite composition and a definite chemical formula.

Among important interstitial compounds is an iron carbide, cementite, Fe_3C, which lends hardness to certain kinds of cast iron and steel (§ 563). But iron nitride, Fe_3N, possesses similar properties and may be made to serve the same ends, in spite of the great contrast between the chemical properties of carbon and nitrogen. Sometimes we meet a combination of an ordinary solid solution and an interstitial solution. In manganese steel, for example, atoms of iron and manganese form the primary crystal lattice, and carbon atoms penetrate into the interstices.

The small atoms of the interstitial elements doubtless establish covalent bonds with surrounding metallic atoms. Thus the number of free electrons is reduced, and electrical conductivity is greatly diminished, in comparison with the pure metal. The interlocking of the atoms in covalent union gives a strong and rigid structure, hence the interstitial compounds have extremely high melting points, and several of them are very nearly as hard as the diamond. The carbides of tungsten, tantalum, and columbium (WC, TaC, CbC), though extremely hard, are very brittle, hence are usually employed as a compressed powder, cemented together with about 13 per cent of cobalt. Tools made of this material will cut hard steel on a lathe, and are so resistant to wear that the loss of time often incurred in keeping tools sharp is very largely avoided.

The post-transition elements (Cu, Zn, etc.) in general do not dissolve appreciable amounts of carbon, either because their atomic radius or crystal structure is unfavorable to the accommodation of carbon atoms between the metallic atoms, or in some instances because the metal or semi-metal is sufficiently rich in valence electrons to combine with itself, forming simple molecules or extended sheets, thus tending to exclude carbon. The alkali and alkaline-earth metals, by contrast, combine with carbon to form definite chemical compounds in which metallic properties disappear. Calcium carbide (§ 450) is an example.

Some Important Alloys

(Composition in percentages by weight)

Low-melting Alloys

Wood's metal 50Bi 25Pb 12.5Sn 12.5Cd — m.p. 65.5°C
Solder 67Pb 33Sn — m.p. 275°C
Type metal, standard 58Pb 26Sn 15Sb 1Cu
Marine babbitt 72Pb 21Sn 7Sb
Gold solder 63Au 23Ag 14Cu
Aluminum solder (Bu.St.SN4) 86Sn 9Zn 5Al
Silver solder 40Ag 40Sn 14Cu 6Zn
Silver solder (hard) 80Ag 13Cu 6.8Zn
Solder (hard yellow) 53Cu 43Zn 1.3Sn 0.3Pb
Gold solder (low melting) 55Ag 29Cu 12Au 5.5Zn
Gold solder (18 carat) 63–75Au 13–31Ag 6.3–12Cu
Babbitt metal 90Sn 7Sb 3Cu

Corrosion-resistant Alloys

Stellite, No. 3 55Co 20–23Cr 15–20W 3–5Fe 1.5–4C
Stainless steel 90–92Fe 8Cr 0.4Mn <0.12C
Monel metal 60Ni 33Cu 6.5Fe
Tantiron, Duriron 85Fe 13.5Si 1C 0.4Mn 0.2P and S
Nichrome castings 60Ni 25Fe 15Cr 0.7C
Illium G 58Ni 22Cr 6–7Cu 4Mo 2W 1Mn 6–7Fe

Light Alloys

Magnalium 70–90Al 10–30Mg d = 2 to 2.5
Lynite 89–95Al 2–14Cu 0.5–1.5Mg <2, all others
Dowmetal A 92Mg 8Al — m.p. 600°C
Dowmetal T 92Mg 3.8Cu 2Cd 0.2Mn

High-resistance Alloys

Manganin 53Cu 39Zn 2.7Sn 2.5Ni 1.7Mn 0.2Al
German silver 52Cu 26Zn 22Ni
Chromel A, Nichrome IV 80Ni 20Cr
Thermocouple 80–100Pt 0–20Rh or Ir

Coinage and Jewelry

U. S. 90Ag 10Cu
Great Britain 92Au 8Cu
Pt substitute 70Ag 25Pt or Pd 5Ni or Co

18-Carat gold 75Au 10–20Ag 5–15Cu
White gold 75–85Au 8–10Ni 2–9Zn

Alloys for Cutting Steel

Carboloy 87WC 13Co
High speed steel 75Fe 18W 6Cr 0.3V 0.7C

Miscellaneous

Dental amalgam 70Hg 30Cu
Type metal 70Pb 18Sb 10Sn 2Cu
Brass, ordinary 67Cu 33Zn
Battery plates 94Pb 6Sb

500. Allotropy

Among non-metals the existence of allotropic forms is ordinarily ascribed merely to differences in crystal structure. The two chief forms of sulfur, for instance, are both constructed with the puckered ring, S_8, as the element of crystal structure (§ 304).

Among the *transition metals*, differences in allotropic form seem frequently to originate in differences in the atom itself. An electron may sometimes be transferred from the outer (valence) shell to an incomplete inner shell or back again without the expenditure of any very considerable quantity of energy. The result is an alteration in atomic radius and in the effective number of valence electrons, hence frequently an alteration in crystal structure.

Industrially important properties of a metal are often greatly altered by a change in allotropic form: Ordinary tin is malleable and ductile, has fair electrical conductivity and a bright metallic luster; but gray tin, stable below 18°C, is lusterless and so brittle as to be practically useless. Block tin, stored in warehouses in severe Russian winters, has sometimes collapsed to a gray powder—an event that nowadays would doubtless be laid at the door of counter-revolutionary plotters. Gray tin, though brittle as chalk, possesses the crystal structure of the diamond. That need not surprise us. The comparatively large size of the tin atom (almost double that of carbon) keeps the atomic centers so far apart that the tetrahedral coordination, so effective in lending hardness to the diamond, leaves tin soft and weak.

Changes in allotropic form are frequently responsible for alterations in *magnetic properties*. In other instances magnetic properties appear to be dependent on covalent linkages between atoms, within the crystal lattice of the solid. Heusler alloys, produced by sudden cooling of $(Cu, Mn)_9Al_4$ from 800°C, apparently owe their strong magnetic properties to a superstructure in which atoms of copper and

manganese alternate in a regular pattern in a lattice of the same type as that possessed by Cu_9Al_4.

The existence of allotropic forms very greatly complicates the study of alloys. In alloys of manganese and iron, for example, three different allotropic forms of manganese and two different forms of iron may appear at different temperatures or when the components are mingled in different proportions. The limits of stability of all these are further altered by carbon, which may penetrate interstitially, or by some other element, such as chromium or titanium, which may replace atoms of iron or manganese in the primary crystal lattice.

501. Effect of Working, Annealing, or Quenching

When a metal is rolled into sheets or drawn into wire the crystals composing it are broken up, and the slip planes between neighboring layers of atoms tend to become blurred. Extreme pressure may so disarrange the atoms as to form a layer of apparently amorphous material between elongated crystal grains. A metal or alloy, of course, becomes less ductile as the result of such mechanical working and frequently is made very brittle. Nevertheless it often gains in tensile strength, since *metals usually break by giving way along natural cleavage planes within their crystal grains, rather than by rupturing the tough, amorphous intercrystalline material.* The tensile strength of tungsten, for example, is so greatly increased by swaging the metallic grains (drawing the material, hot, through a die) that the finished product, an incandescent-light filament, has a tensile strength exceeding that of steel.

When a *nearly pure metal*, such as copper or platinum, has been rendered brittle by mechanical working it may be rendered *soft* and *ductile* by heating it to a very high temperature, then suddenly *quenching* it in water or oil. When heated, the atoms tend to regain the ordered arrangement characteristic of a crystal, and strains tend to be relieved. The subsequent sudden cooling hinders the separation of impurities (cupric oxide, for example) that would otherwise render the metal brittle.

An *alloy*, however, is frequently *hardened* by being heated to a high temperature, then suddenly cooled, especially if carbon or some other element is present that can penetrate the crystal lattice to form an interstitial solution. The high temperature lends sufficient mobility to the atoms to permit the interstitial solution to be formed; subsequent sudden cooling freezes the assemblage of atoms into comparative immobility and so maintains the interstitial structure down

to temperatures at which it would otherwise collapse, expelling carbon. Further details on the way in which this works out in the *heat treatment* of iron and steel will be given in § 563.

Traces of impurities (oxides, sulfides, etc.) in metals or alloys usually tend to separate between the crystalline grains, often greatly weakening the material. A trace of beryllium oxide, BeO, in metallic beryllium renders the metal almost worthless unless special precautions are taken to insure complete deoxidation. Traces of sulfur or phosphorus greatly weaken steel. Sometimes this separation of impurities takes place gradually at room temperature, after the material has been rolled or cast. The result is "age hardening," which sometimes goes so far as to make the material very brittle.

502. What Happens When Metals Rust or Corrode?

The usefulness of metals is limited by their tendency to rust or corrode. Losses due to these processes amount to many million dollars each year, in spite of all efforts. *Rusting or corrosion consists fundamentally of the loss of electrons by a metal, the metal passing into solution as ions:*

$$Al \rightarrow Al^{+3} + 3e$$

If the metal has more than one valence, ions of the lower valence will be formed:

$$Fe \rightarrow Fe^{++} + 2e$$

The higher the position of the metal in the electrochemical series the greater is the tendency for corrosion to take place, when conditions are favorable to corrosion.

Nevertheless, *corrosion will not occur unless some reducible substance is in contact with the metal, at the point of corrosion or at some distant point, to receive the electrons set free.* Commonly this reducible substance is either:

1. *Oxonium ion*, H_3O^+, which is reduced to *hydrogen gas:*

$$2H_3O^+ + 2e \rightarrow 2H_2O + 2H$$
$$\hookrightarrow H_2$$

or else,

2. *Oxygen gas* and *oxonium ion*, reduced jointly, forming *water:*

$$O_2 + 4H_3O^+ + 4e \rightarrow 6H_2O$$

Observe that the solution becomes less acid as a result of either of these two reactions.

The first reaction, *liberation of hydrogen*, occurs in solutions that are distinctly acid; it occurs more readily with some metals than with others. *With iron and steel, liberation of hydrogen will occur only if the hydrogen ion activity is greater than that corresponding to a pH* (§ 405) *of about* 4.3.

The second reaction, *absorption of oxygen*, may occur even in solutions that are neutral or alkaline, if plenty of oxygen is available. Iron and steel will not rust or corrode appreciably in water that is neutral or even very faintly acid, if air or oxygen is excluded.

503. Part Played by Surface Films in Corrosion

Certain metals (chromium and aluminum, for example), if very pure, soon become covered with a closely adhering, continuous film of oxide, when they are exposed to moist air. The oxide film protects

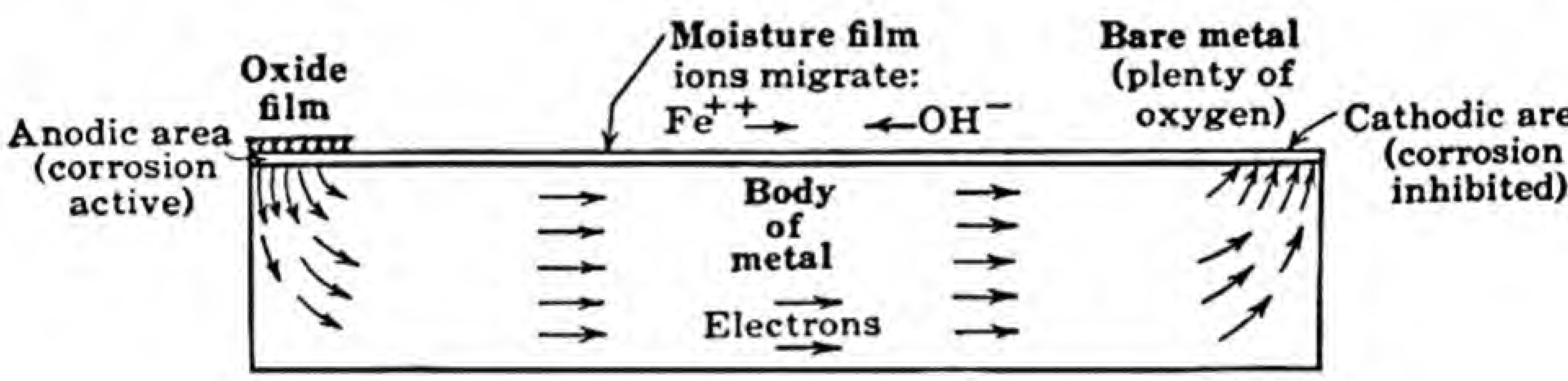


FIG. 155. Corrosion as an electrochemical process.

them from further corrosion, under conditions in which the film is stable. These films can be separated from the underlying metal in various ways and made visible, though their thickness, with iron, is only about 0.46×10^{-5} cm.

This surface film of oxide is present on samples of iron and steel that have been exposed, even momentarily, to moist air. Unfortunately it is rarely sufficiently dense or continuous to protect the underlying metal. On the contrary it acts to accelerate corrosion. The oxide film is fractured or porous in certain places. Here oxygen penetrates and accepts electrons, as shown in Fig. 155. These portions of the surface therefore act as *cathodes*.

In other places, where the oxide film is denser or more nearly continuous, moisture penetrates through the film to the metallic surface, but the diffusion of oxygen to the surface is impeded. These portions of the surface therefore become *anodes*, metallic atoms here passing into solution as ions, and releasing electrons, which are carried through the body of the metal to the spots that serve as cathodes.

We see that *oxygen is necessary to corrosion, yet corrosion occurs at the parts of the metallic surface where the supply of oxygen is the most limited.*

The coating that we call "rust" is formed on iron and steel in a somewhat complicated manner. Ferrous ions, Fe^{++}, are produced at the anode, directly from the metal, but are readily oxidized to the ferric condition, wherever oxygen penetrates:

$$4Fe^{++} + O_2 + 2H_2O \rightarrow 4Fe^{+3} + 4OH^-$$

Fe^{++} and Fe^{+3}, moving toward the cathode, encounter OH^-, moving in the opposite direction (see Fig. 155). The result is the precipitation of a mixture of ferrous and ferric hydroxides, which by the action of carbon dioxide of the atmosphere gradually becomes converted into hydroxy-carbonates. This mixture is a *rust spot*. The iron beneath it becomes anode, as we have just seen, continuously passing into solution as Fe^{++}. So the corrosion digs deeper and deeper beneath the spot of rust, the pit thus formed being filled by ferrous and ferric hydroxides and hydroxy-salts of whatever anions happen to be present in the solution or moisture film. No wonder that common speech has it that "rust begets rust"! (Ex. 8, 9.)

504. Other Factors Influencing Corrosion

Since corrosion is an electrochemical process, the rate of corrosion of any metal in any situation will be determined by all the conditions that determine the strength of the electric current which accompanies the corrosion:

1. In some instances metallic atoms may react directly with water molecules to produce a coating of hydrous oxide. Representing a divalent metal by M:

$$M + 2H_2O \rightarrow \underset{\text{Hydrous oxide}}{M(OH)_2} + 2H \text{ (adsorbed)}$$

Corrosion may then depend not only on the access of sufficient oxygen to clear away the adsorbed film of hydrogen but on the presence of substances in the solution that peptize or disperse the hydrous oxide coating, and thus expose a new portion of the metal.

2. *Undissolved impurities* in the metal usually influence corrosion. Any impurity that can act as cathode will accelerate corrosion in surrounding portions of metal, which become anodes. Particles of graphite have this effect. Particles of sulfide or slag impurities in iron and steel, under mildly corrosive conditions, also usually induce corrosion in their neighborhood.

3. *Ionic compounds* in general, dissolved in the solution or in the moisture film, tend to increase corrosion, since their presence makes

the solution a better conductor of electricity. This is one reason why sea water is especially corrosive, though some allowance must be made for acid set free by the hydrolysis of magnesium salts (§ 396).

4. *Strains or minute cracks set up in working the metal* (stamping, rolling, or wire-drawing) produce anodic and cathodic portions. Minute cracks or scratches, too fine to be seen, even with a microscope, produce anodic areas at the bottom of each crack or scratch, since oxygen, diffusing downward through the solution, may all be used in oxidizing Fe^{++} to Fe^{+3} before it reaches these areas. A well-polished metal is slow to corrode, since the minute cracks are either removed or filled up in the polishing.

5. *Water in motion* will bring oxygen to the cathodic surfaces faster than this could happen by diffusion alone, and tends to remove the reaction product, Fe^{++}. Both effects favor corrosion.

6. If a solution wetting a metal is *more concentrated in one spot than another* (perhaps as the result of evaporation) this in itself will set up a flow of current (§ 512) and so accelerate corrosion.

7. *Alternate wetting and drying* tends to disrupt the film of rust or oxide, and so favors corrosion.

8. Any substance that can form a *complex ion* with the cation of the corroding metal will decrease the concentration of the cation and so (by mass action) will aid corrosion. We may probably thus account for the marked corrosion of tin by citric and oxalic acids.

9. Many metals (especially iron, nickel, and chromium) acquire *a very temporary and unreliable protection* against corrosion by being made *passive*, presumably owing to an invisible oxide film, readily formed (1) by dipping the metal into strong nitric acid or a dilute solution of nitric acid in alcohol or (2) by making it anode in an alkaline solution or acid dichromate solution. The passivity may be destroyed by a blow or by scratching the film at any point, or by certain ions, particularly Cl^- and Br^-.

505. How to Minimize Rusting and Corrosion

From all that has just been said we may easily infer what sort of measures will best serve to minimize rusting and corrosion:

1. The metal should be of uniform composition, homogeneous, and free from mechanical strains.

2. It should be protected against stray currents of electricity.

3. If its surface is bare it should not be in direct contact with carbon, copper, tin, or any other element below itself, in the electrochem-

ical series. On the other hand, if it is in contact with metals having a higher position than itself (zinc or aluminum in the case of iron), the corrosion will usually all fall on the metal occupying the higher position. This principle is sometimes employed in protecting boilers, by placing chunks of zinc inside them. (Ex. 10.)

4. Water that is to be passed through iron pipes becomes less corrosive if dissolved air is first removed, by heating or otherwise.

5. Where the cost is not too great, steel may be made more resistant to corrosion by alloying with nickel. A few hundredths of 1 per cent of copper is a protection to sheet steel, for reasons not yet well understood. Corrosion-resistant alloys of many kinds have been developed for special uses. Nevertheless no metal or alloy is known that will resist corrosion under all conditions.

6. Where permissible, the metallic surface should be covered with *a water-tight coating.* This must be in actual contact with the iron, if the film of moisture responsible for corrosion is to be excluded. It follows that the surface to be protected must be thoroughly cleaned, and free from rust.

506. Protective Coatings for Metals

The protective coatings used on metals include (1) paints, varnishes, and lacquers; (2) enamels, which are really glassy coatings, adhering to a carefully cleaned metallic surface; (3) coatings produced by the alteration of the surface of the metal itself; (4) other metals.

An example of protection by surface alteration is *Russian iron*, made by exposing sheet iron to superheated steam, which gives it a closely adherent black film of magnetic iron oxide, Fe_3O_4. In the *Parker process* the steel is dipped for a short time into a boiling, strongly alkaline solution of sodium phosphate. This covers the surface with an almost invisible gray coating, presumed to be a ferrous oxyphosphate. Rifles are commonly so treated, and many typewriter and automobile parts, previous to enameling.

Metallic films are sometimes produced by electrolytic deposition (Ni, Cr, Cd), sometimes by dipping into a bath of molten metal (Zn, Sn), and sometimes by spraying molten metal, atomized in a blast of air (*Shoop process:* Pb, Cu, Ni, and others).

Galvanized iron is sheet iron that has been carefully cleaned, then dipped into molten zinc. Sheet iron is also frequently coated with zinc by electrodeposition ("electro-galvanizing"). *Calorized iron* is heated in air-tight drums in contact with zinc dust, until a thin coating of iron-zinc alloy has been produced.

507. Metallurgy

The minerals that serve as ores of the important heavy metals are usually found in nature in admixture with useless impurities, collectively known as *gangue.* The ore particles are fortunately often very much heavier than the accompanying gangue, hence may be separated by crushing the ore to a fine powder, then washing away the gangue in a current of water—frequently with elaborate precautions to permit the settling and subsequent recovery of the ore particles. Sometimes the heavy ore particles may be separated from gangue by settling from an air current, as in separating grain from chaff. Occasionally the ore particles more readily acquire an electric charge than the gangue particles or may be separated by a magnet.

Still more important is *froth flotation.* The finely powdered ore is churned up with water containing several pounds of creosote oil or pine oil for each ton of ore. Air is blown through the mixture, forming a froth that consists of innumerable bubbles, each stabilized by a thin film of oil. It happens that the valuable constituents of ore (usually free metal or a metallic sulfide) are more easily wet by the oil than the siliceous part, or gangue. The gangue settles to the bottom, but the ore particles are drawn into the film of oil surrounding the rising air bubbles, or into the surface separating oil from water. Each bubble is thus, in effect, "armorplated" by a layer of ore particles, and the stability of the foam is very much increased. If the process is carried out with care as much as 90 per cent of the heavy metal in the ore will be found in the froth; and the material to be treated in the subsequent smelting process may be reduced to a fifteenth of its original bulk.

The concentrated ore, by whatever process obtained, may still need further purification by *roasting* in a current of air. Arsenic, sulfur, and sometimes other impurities are thus oxidized and removed, carbonates being concurrently decomposed. In this manner a heavy metal is ordinarily converted into an oxide, which may then be reduced to metal, very frequently by being heated with *coke* (carbon) in a furnace. The actual reducing agent is carbon monoxide. Sometimes a *metallic sulfide,* present in an incompletely roasted ore, serves as a reducing agent, reducing oxide to metal. A few metals (iron, copper, lead, tin, etc.) melt and may be drawn from the bottom of the furnace in a liquid condition.

Whenever a metal would be injured by acquiring carbon as an impurity, reduction from an oxide ore is commonly accomplished with the aid of a more active metal. Carbon-free manganese, chromium, iron, and alloys of these with one another are readily obtained by reaction of

their oxides with powdered metallic aluminum. When the mixture is ignited the aluminum combines with the oxygen, forming aluminum oxide and setting the heavy metal free:

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3 + 208{,}300 \text{ cal}$$

So much heat is released that the iron (or other heavy metal) melts and collects in the bottom of the crucible beneath a protective layer of molten aluminum oxide. This is the famous *thermite process*. It is also widely used for welding heavy castings, since molten iron can thus be produced at so high a temperature that its admission into a fracture will cause neighboring portions of the fractured metal to melt and mingle with the iron admitted.

The methods just described apply chiefly to the winning of the heavy metals. The alkali and alkaline-earth metals and aluminum are commonly prepared by *electrolysis*, for more energy needs to be expended to reduce them from their ores than the oxidation of carbon monoxide is able to supply.

Technical Words

Slip planes—planes along which a solid will yield or flow when a high pressure is applied.

Superconductivity—the nearly perfect electrical conductivity that a few metals show at temperatures near absolute zero, p. 576.

Alloy, p. 578. **Intermediate phase**, p. 579.

Intermetallic compound—a name frequently given to any alloy intermediate phase of nearly constant composition.

Superstructure—a type of solid solution in which two different types of atoms alternate, instead of assuming random positions in the crystal lattice.

Interstitial solution or **interstitial compound**, p. 583.

Mechanical working—an operation (such as rolling, stamping, or drawing) by which the shape of a metal or alloy is altered and usually also its mechanical properties.

Annealing—softening a metal or alloy by heating, followed by slow cooling to room temperature.

Tempering—altering the properties of a metal or alloy by heating, followed by slow cooling through a specified temperature range.

Quenching—sudden cooling of a heated metal or alloy, commonly by plunging it into oil or water or by a blast of cold air.

Heat treatment—any combination of tempering, quenching, and annealing by which the physical properties of a metal or alloy may be altered.

Passive condition, p. 590. **Metallurgy**, p. 367. **Roasting**, p. 368. **Flux**, p. 516.

Gangue—waste material, separated and discarded in preliminary operations preceding the actual *smelting* of an ore.

Froth flotation—a process for separating suspended ore particles from particles of gangue, with the aid of a froth or foam that carries the ore particles away while the gangue particles settle.

Thermite process—the reduction of iron and other heavy metals from their oxide ores, using aluminum (or occasionally some other light metal, such as magnesium or calcium) as a reducing agent.

EXERCISES

1. By reference to the Periodic Table, facing the back cover of this book, determine which of the transition metals differ from the rest in having only one electron in the highest energy level.

2. How does the manner in which a current is conducted in a solution differ from its conduction in a metal?

3. What is meant by atomic heat capacity? What value does it usually have for solid elements at ordinary temperatures?

4. A few metals seem to possess directed valence bonds linking neighboring atoms. Would such a metal have less or more than normal conductivity? Why?

5. Check the statement made in the text (§ 497) with regard to the proportion in which aluminum and silicon atoms need to be intermingled with copper atoms to obtain an electron-atom ratio 1.4:1.

6. In an alloy of zinc and platinum how many atoms of platinum (zero-valent) must be present for every 100 atoms of both metals to make the electron-atom ratio 1.4? 300

7. Show that γ-brass and four other intermetallic compounds mentioned (§ 498) all possess an electron-atom ratio of 21:13.

8. A piece of string is wrapped around the middle of a clean iron nail and the nail is dropped into water. Where will corrosion proceed most rapidly? Why?

9. A sheet-iron tank full of water was found to corrode most rapidly beneath droplets of oil, which had entered with the water and collected on the walls of the tank. Explain.

10. Explain why builders should never support copper eave troughs directly on iron brackets.

Chapter 37

ELECTROCHEMISTRY

508. The Development of Electrochemistry

The story of electrochemistry takes us back to the early days of electrical experimentation, when Galvani, in Italy, was watching the nervous twitchings of frogs' legs, stimulated by electrical discharges (1790), and Franklin, in America, was drawing electricity from a thundercloud down a wet kite string (1752). These experiments, and others that followed, showed that electrical phenomena of different kinds are really closely related. Electricity causes definite effects according to definite laws, whether it is produced by rubbing a rod of sealing-wax with silk, by air currents in a thundercloud, by chemical action, by heat, by movement of an electrical conductor in a magnetic field, or by the "living dynamo" of the electric eel.

With convenient means for producing electric currents by chemical action (§ 511), practical chemical applications were not long delayed. Nicholson and Carlisle, in England (1800), decomposed water by the electric current. Then Sir Humphry Davy produced metallic sodium and potassium (1807) and several other new metals by electrolysis (§ 525). Oersted, Faraday, Maxwell, Kelvin, and others made discoveries and formulated laws that rendered progress secure and rapid in the decades that followed.

Moissan, in France (1886), succeeded in producing elementary fluorine by electrolysis; while metallic aluminum (1886), electrolytic copper (§ 522), calcium carbide (§ 450), and many other electrochemical products became important commercial commodities. These developments appeared in a generation that witnessed the invention of the first practical electric dynamo (1870), the telephone (1876), carbon arc and incandescent lighting (1878), and the electric railway. The apparently trivial experiments of the preceding century, with frogs' legs, kites, and rods of sealing-wax, had laid the foundations of a great science, which altered the whole aspect of civilization.

The electrochemical industries of today owe much to the fundamental discoveries of Faraday, which occupied him for nearly twenty years, during which time he discovered the principle of induction that is the basis of the modern dynamo and the law of electrolysis that bears his name (§ 523). The impressive industrial developments that rest upon these researches are widely distributed, and many countries have contributed to them.

509. Electrothermics

In the applications of electricity in the chemical industries, the electrical current often serves as a mere source of heat. This is the field of *electrothermics*. Examples are the production in electric furnaces of silicon carbide, aluminum oxide abrasives, calcium carbide, carbon disulfide, electric steel, ferroalloys, and the reduction of tungsten and molybdenum from their oxides in small electric furnaces in a current of hydrogen.

Furnaces in which the electric current supplies heat for a chemical reaction are of four main types:

1. *Arc furnaces*, in which an arc is struck between two electrodes or between several electrodes and a pool of molten metal or carbide.

2. *Granular resistor furnaces*, in which the charge consists of granules of some material, such as graphitized carbon, that is raised to incandescence by the passage of the current.

3. *Induction furnaces*, in which a high-frequency current induces a current that generates heat in a metallic charge, without the use of any electrodes at all.

4. Small *wire-wound* furnaces, in which a tube of aluminum oxide or similar refractory material is wound with nickel-chromium alloy wire (Nichrome or Chromel) or (for very high temperatures) with tungsten or molybdenum.

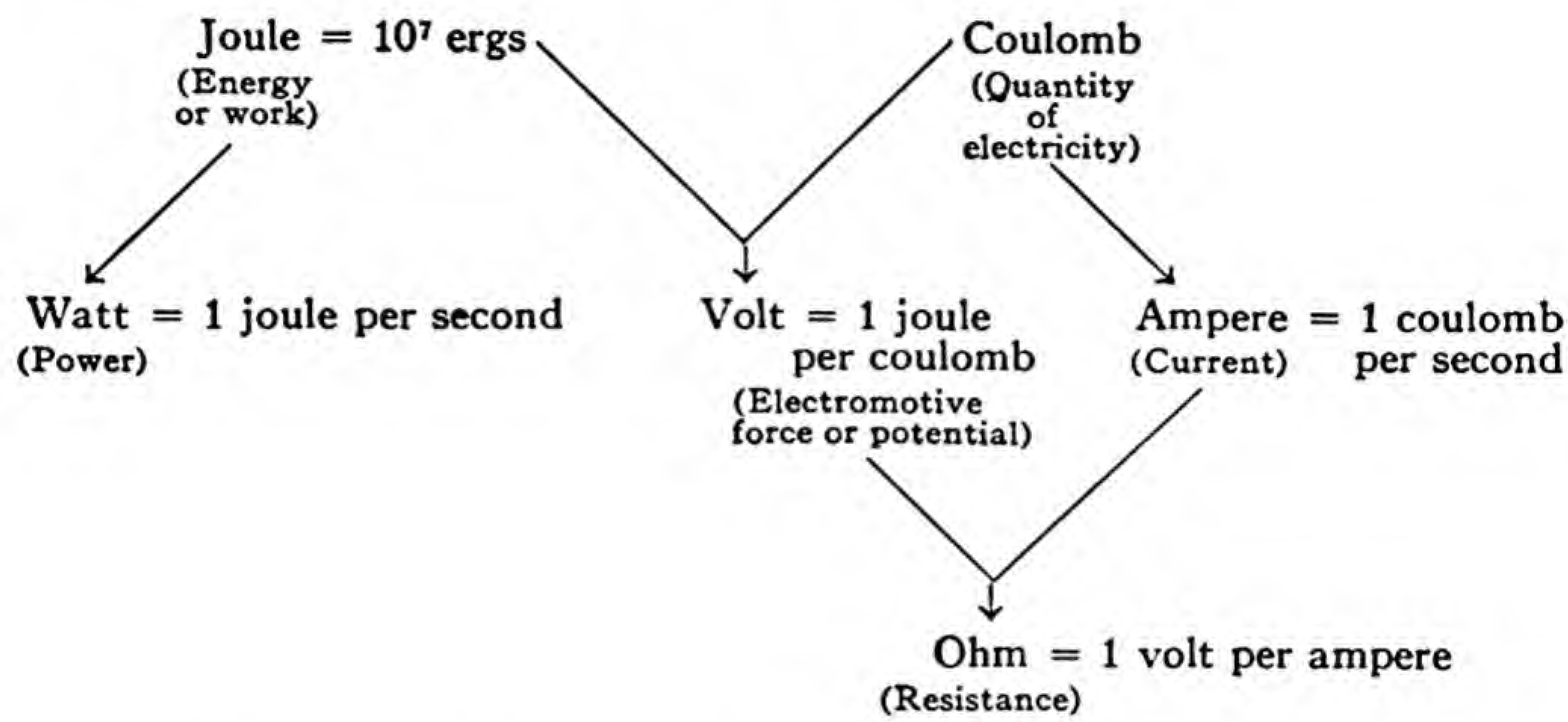
Important products of the electrothermic industry are the chief *abrasives* (substances of extreme hardness, which are used in grinding machine parts to exact dimensions. One of these is silicon carbide, SiC (trade-names: Crystolon and Carborundum). It owes its hardness to the fact that it has the very structure of the diamond (§ 441) except that every other atom is one of silicon. Another important abrasive is a dense form of aluminum oxide (trade-name: Alundum).

510. Electrical Units

The electrical units in most common use are best defined by starting with the *joule*, the unit of *work*. This is 10^7 ergs. A person of average

weight climbing an average stairway performs about 100 to 150 joules of work with each step. (Ex. 1.)

The unit of *power* (rate of doing work) is the *watt*. This is work done at the rate of 1 joule per second. A horsepower is 746 watts. One would do work at the rate of 1 horsepower if he could run up a stairway at a speed of 5 or 6 stairs a second. (Ex. 2.)



The unit of *electrical quantity* is the *coulomb*. This is the quantity of electricity that will deposit 0.001118 gram of metallic silver on the cathode, when a current is passed through a solution of silver nitrate in a *silver coulometer* (Fig. 156), under conditions that are carefully controlled (to insure that the deposit is really pure silver, and that the deposition of silver is the only reaction taking place at the cathode).[1] A coulomb represents the quantity of electricity carried by about 6.24×10^{18} electrons. (Ex. 3.)

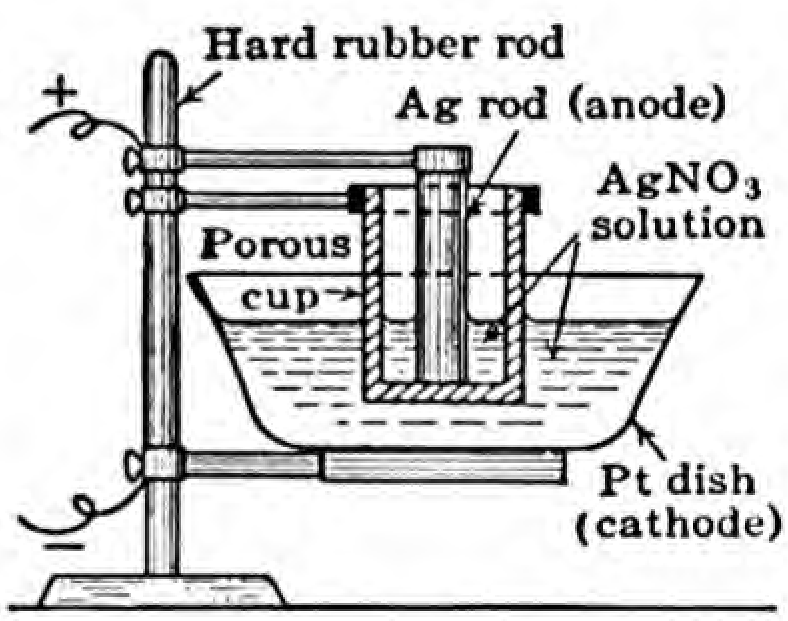


FIG. 156. The silver coulometer.

The unit of *electrical current* is the *ampere*. This is a current such that 1 coulomb of electricity is transferred past each point of an electric circuit during each second that the current flows. The reader may have observed that the headlights of his automobile draw about 15 amperes. To start the motor, over a hundred amperes may be needed. This is so large a current that it

[1] This is the *international coulomb*. It is intended to be identical with the *theoretical coulomb*, defined in terms of a unit magnetic pole, which in turn derives from the centimeter, gram, and second (see textbooks of physics).

is shunted around the instrument board and does not register on the ammeter. (Ex. 4.)

To produce an electric current, that is, to set electrons in motion, we commonly use either an *electric generator*, often called a *dynamo* (loops of wire, whirling in a magnetic field), or an *electrochemical cell* (such as a dry cell, § 513, or a storage cell, § 514). *Different sources of current differ greatly in the energy with which they may impel the electrons to move.* Any source that can confer 1 joule of energy on each coulomb of electricity set in motion is said to have an *electromotive force* (or, colloquially, a "voltage") of 1 *volt*. (Ex. 5, 6.)

Whenever 1 joule of energy is expended for each coulomb of current passing *between two points of a circuit*, the two points are said to have a

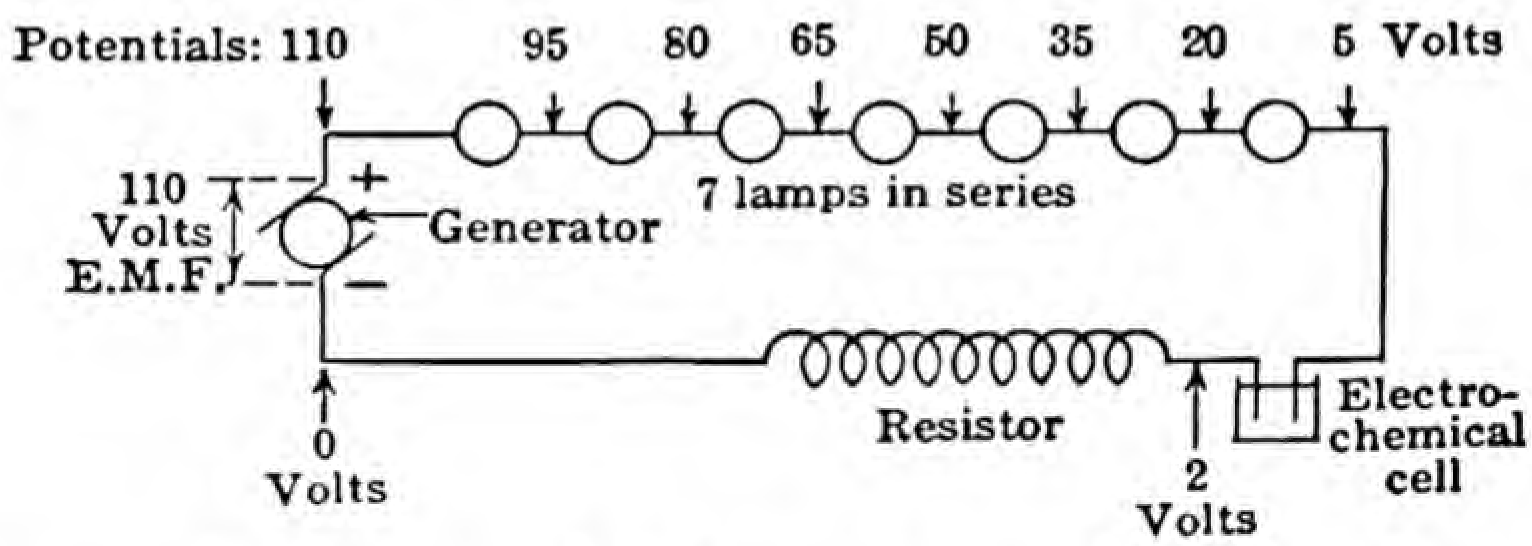


FIG. 157. The sum of the potential differences, around a circuit, is the electromotive force of the generator or battery that serves as a source of current.

difference of potential of 1 volt (the more positive point being arbitrarily assigned the higher potential). Adding differences of potential in volts, along a circuit, from the negative to the positive terminal of a source of current, we get the total energy in joules expended in the circuit for each coulomb passed through it. This is the electromotive force of the source of current (Fig. 157). (Ex. 7.)

The energy expended within an electric circuit may all be expended as *heat;* or a part of it may be expended as *mechanical energy* (in turning an electric motor), as *electromagnetic energy* (in magnetizing an electromagnet), or as *chemical energy* (in electrolysis, whenever a current passes through a solution or a molten salt). *For the special case in which all the energy in some part of the circuit is expended as heat,* we say that this part of the circuit has a *resistance* of 1 *ohm* if a difference of potential of 1 volt between its two ends maintains a current of 1 ampere. Ohm's Law (current, in amperes = potential difference, in volts ÷ resistance, in ohms) holds for this special case, not otherwise. So be on your guard against misapplying the law. (Ex. 8.)

These definitions (except for the coulomb) have been worded in such a way as to show the relationship of the units to each other and their derivation from the joule and erg (which in turn derive from the

centimeter, gram, and second, p. 724). Each quantity must be defined in terms of those already defined; to define the volt in terms of the ampere and ohm is to reason in a circle. (Ex. 9.)

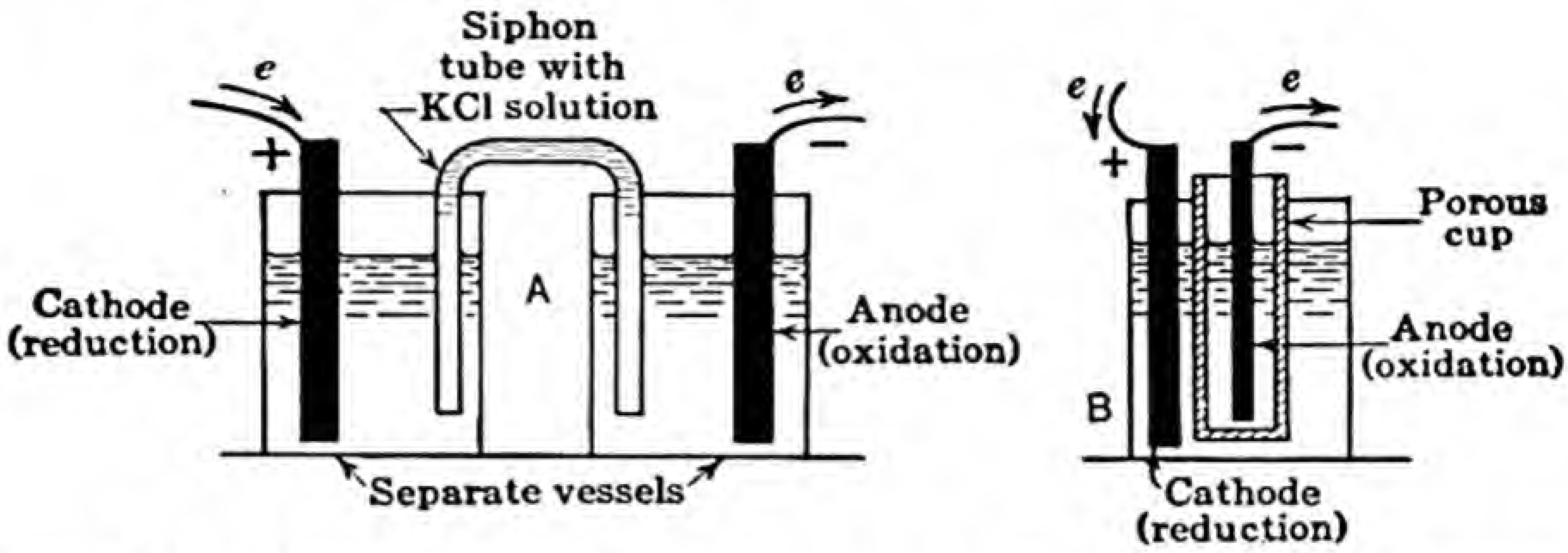


FIG. 158. How a chemical reaction may induce a flow of electricity.

511. How a Chemical Reaction May Produce a Current

To obtain an electric current from a chemical reaction we must have:

1. An *oxidizable substance* (reducing agent); in other words, one that readily loses electrons.

2. A *reducible substance* (oxidizing agent); in other words, one that readily gains electrons.

We must then arrange that electrons lost by the oxidizable substance must pass through a wire on their way to be accepted by the reducible substance. This ordinarily means that the two substances must *not* be placed in contact. We must have them in separate vessels, joined by a liquid conductor, such as a solution of some salt (*A*, Fig. 158); or we must separate them (*B*) by a porous clay cup or a sheet of some material readily permeable by water.

Nevertheless *zinc*, serving as an oxidizable substance, and *dilute sulfuric acid*, serving as a reducible substance, may be placed in contact in the same vessel, provided that the zinc is *amalgamated* (covered with a thin coating of mercury).[2] We then have a simple electrochemical cell, consisting of a zinc rod and a carbon (graphite) rod, dipping into a solution of sulfuric acid (Fig. 159). Zinc is a readily oxidizable substance. Its

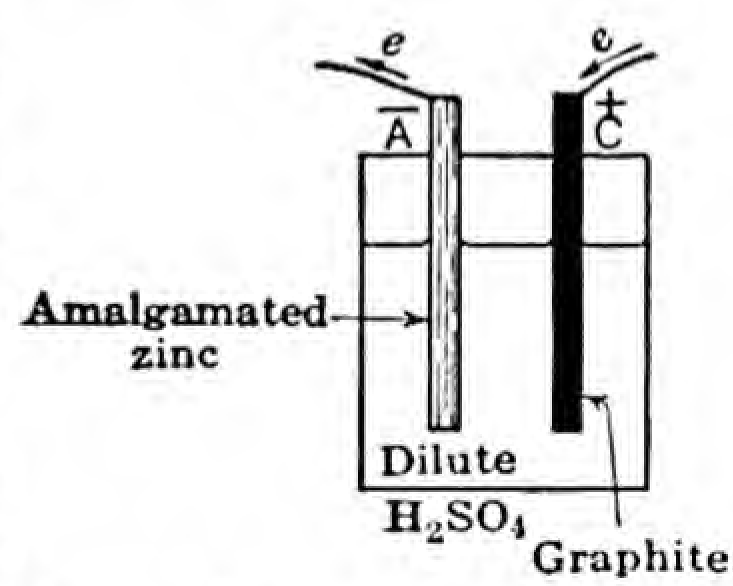


FIG. 159. A simple electrochemical cell.

[2] The mercury prevents the zinc from reacting with the acid prior to closing the circuit. This is partly owing to the fact that the mercury covers over specks of surface impurities in the zinc, which otherwise would form a couple (§ 516) and assist the reaction; but more important is the fact that *extra energy* is needed to liberate hydrogen at the surface of mercury, as compared with the surface of zinc.

atoms lose electrons, being converted into zinc ions, which pass into solution:

$$Zn \rightarrow Zn^{++} + 2e$$

The electrons thus set free tend to accumulate in the zinc electrode, charging it negatively. But the moment the outer circuit is closed the electrons stream through it, enter the carbon electrode, and are there accepted by the oxonium ions of the acid:

$$2H_3O^+ + 2e \rightarrow 2H_2O + 2H \hookrightarrow H_2 \uparrow$$

The result is hydrogen gas, which is evolved from the surface of the *carbon*, in spite of the fact that it is not carbon, but zinc, which is reacting with the acid. Since the zinc electrode is *oxidized*, it is the *anode* (§ 260). Since oxonium ions, at the surface of the carbon, are *reduced* to hydrogen gas, the carbon is the *cathode*. (Ex. 10.)

512. A Concentration Cell

In Fig. 160 a rod of tin has been placed in a bottle containing a fairly concentrated solution of stannous chloride, overlayered with a more dilute solution. Very promptly, mossy crystals of metallic tin will begin to be deposited on the part of the rod that is in contact with the more concentrated solution. The action will continue until the two concentrations have become equal. This is a *concentration cell*—an electrochemical cell in which a flow of current is produced as the result of a difference in concentration between different parts of a solution. Metallic tin, in the more dilute solution, serves as *anode*, passing into solution to form stannous ions:

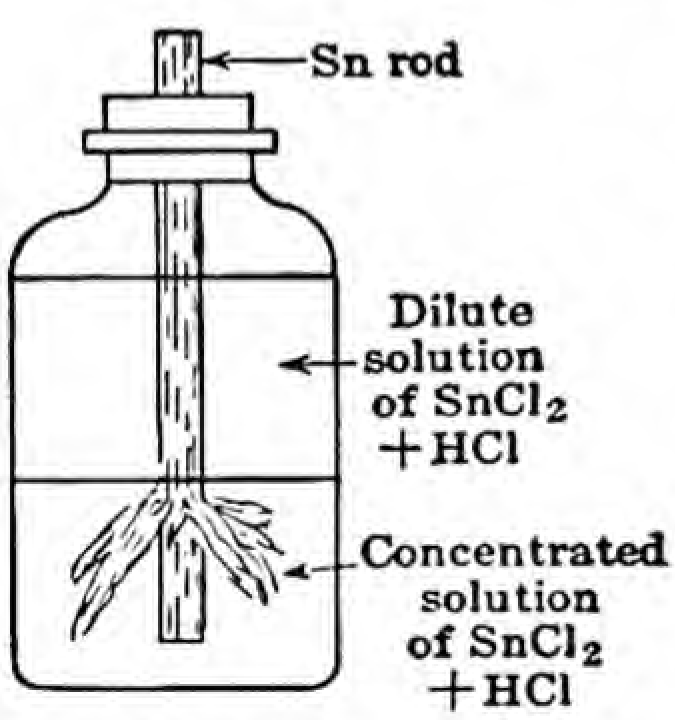


FIG. 160. A concentration cell.

$$Sn \rightarrow Sn^{++} + 2e$$

In the more concentrated solution this reaction is exactly reversed, tin being deposited. Thus the dilute solution becomes more concentrated and the concentrated solution becomes more dilute. When the two concentrations have become equal the flow of current ceases.

This simple experiment shows that metallic tin, in contact with a very *dilute* solution of stannous ions, has a much greater tendency to

lose electrons than one in contact with a *concentrated* solution. Otherwise expressed, the reversible reaction

$$\underset{\substack{\text{More con-}\\\text{centrated}\\ Sn^{++}\\\text{solution}}}{Sn \overset{\substack{\text{Dilute}\\ Sn^{++}\\\text{solution}}}{\rightleftharpoons}} Sn^{++} + 2e$$

tends to proceed toward the right when Sn^{++} is present in a low concentration and toward the left when it is in a high concentration. All this might have been anticipated from the Principle of Mass Action (§ 338). (Ex. 11.)

513. Some Commercial Primary Cells

Electrochemical cells in which a chemical reaction produces a current are sometimes called *primary cells* to distinguish them from *secondary cells*, in which a current, supplied from an outside source, induces a chemical reaction (electrolysis).

The primary cells described in the two preceding pages were intended merely to illustrate principles and are of no practical importance. A serious difficulty with many primary cells is that hydrogen liberated at the cathode soon coats the cathode with a layer of bubbles, and seriously diminishes the surface at which electrons may be accepted. This "polarization" has the effect of an increased resistance to the flow of the current. The obvious remedy is to place some readily reducible substance, namely some good oxidizing agent, in contact with the cathode.

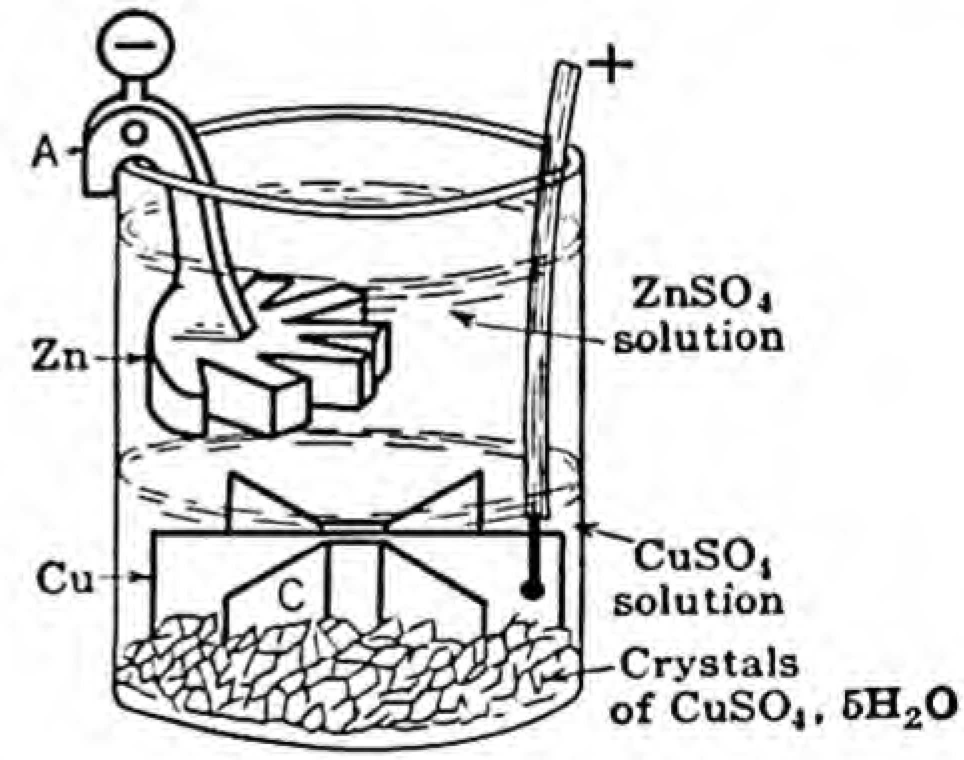


FIG. 161. The gravity cell.

Such a *depolarizer* accepts electrons more readily than the oxonium ions of the solution, hence is itself reduced, thus preventing the liberation of hydrogen gas at the surface of the cathode. Depolarizers that have been used, in different types of cells, include HNO_3, $K_2Cr_2O_7$, $CuSO_4$, CuO, MnO_2.

Of historical interest is the *gravity cell* (Fig. 161), which supplied telegraph lines with current in days of the stage coach and pony express. The cathode, *C*, was a strip of metallic copper in the bottom of the vessel, in contact with a saturated solution of copper sulfate

and undissolved copper sulfate crystals. Over this was layered a lighter solution of zinc sulfate, into which dipped the anode, *A*, a "crowfoot" of metallic zinc. When the circuit was closed metallic zinc passed into solution at the anode and metallic copper was deposited on the cathode:

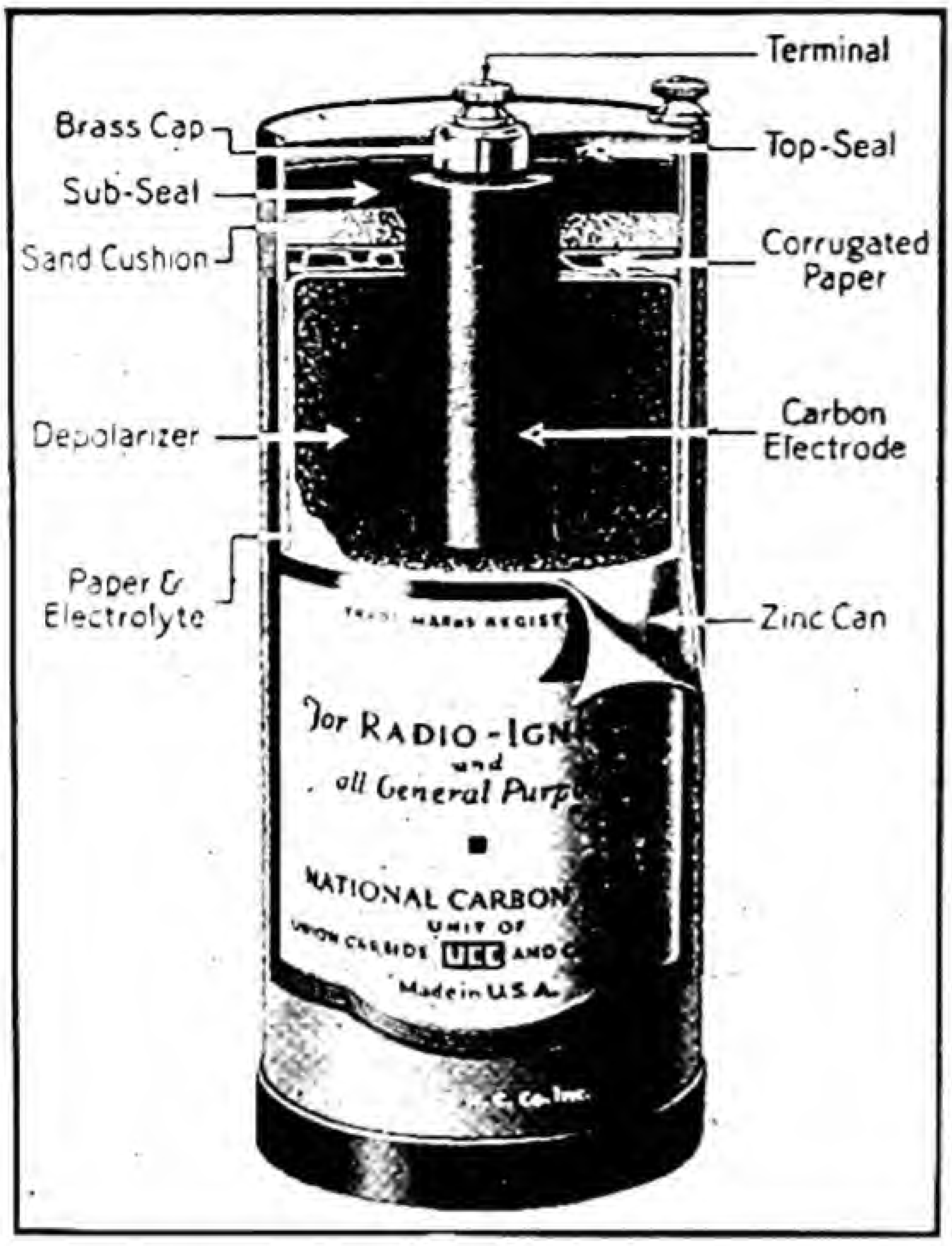


FIG. 162. The dry cell.

$$Zn \rightarrow Zn^{++} + 2e \quad \text{(anode)}$$

$$Cu^{++} + 2e \rightarrow Cu \quad \text{(cathode)}$$

The combined reaction is the same as if a stick of zinc had been directly inserted into a solution of copper sulfate, displacing copper:

$$Zn + Cu^{++} \xrightarrow{2e} Zn^{++} + Cu$$

Such a direct action would, of course, produce no current, since the electrons transferred would not be compelled to pass through a connecting wire.

The most important primary cell of the present day is the *dry cell* (Fig. 162). The anode is a can of amalgamated sheet zinc; the cathode, a carbon rod; the depolarizer, manganese dioxide, with graphite powder and solid ammonium chloride; the electrolyte, a solution of ammonium chloride and zinc chloride in water. When the current passes, zinc dissolves to form Zn^{++} and the manganese is reduced to a lower oxide, probably Mn_2O_3:

$$2NH_4^+ + 2MnO_2 + 2e \rightarrow 2NH_3 + H_2O + Mn_2O_3$$

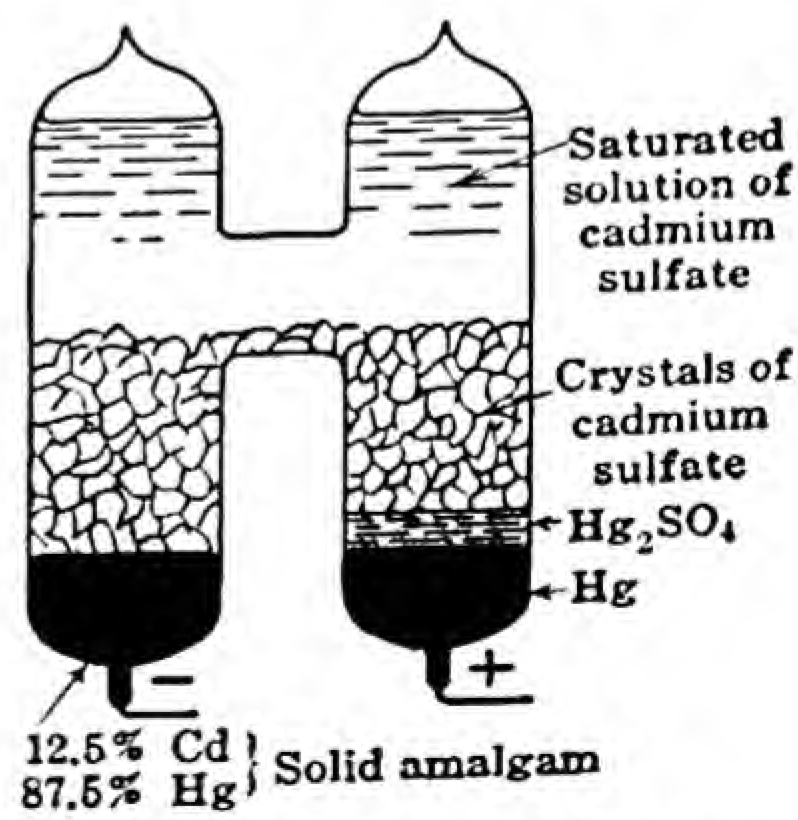


FIG. 163. The Weston standard cell.

The ammonia gas liberated combines with the Zn^{++} to form a complex ion, $Zn(NH_3)_4^{++}$ (an ammine, § 364). If more than a moderate current is drawn continuously from a dry cell the cell will polarize, in spite of the presence of the manganese dioxide.

In the *Weston standard cell* (Fig. 163) the anode is an amalgam of cadmium and mercury; the anode solution, a saturated solution of cadmium sulfate; the cathode solution, a saturated solution of cadmium sulfate and mercurous sulfate; the cathode, metallic mercury, covered with a paste of mercurous sulfate. The electromotive force of this cell has a definite value (1.0183 volts at 20°C), which is practically unaffected by slight changes in temperature. This fact makes the Weston cell a valuable standard for determining the electromotive forces of other cells. It is never used as a source of current and would soon be ruined if an appreciable current were drawn from it. (Ex. 12.)

514. The Lead Accumulator or Storage Cell

The lead accumulator (Fig. 164) is the most important example of a reversible electrochemical cell or "storage cell." The plates are networks of lead-antimony alloy, packed full of *spongy lead* and *lead dioxide*, respectively. During discharge both electrodes become covered with a deposit of *lead sulfate;* but when a current is sent through the cell in the opposite direction, the reactions at the electrodes are reversed, and the plates restored to their original condition:

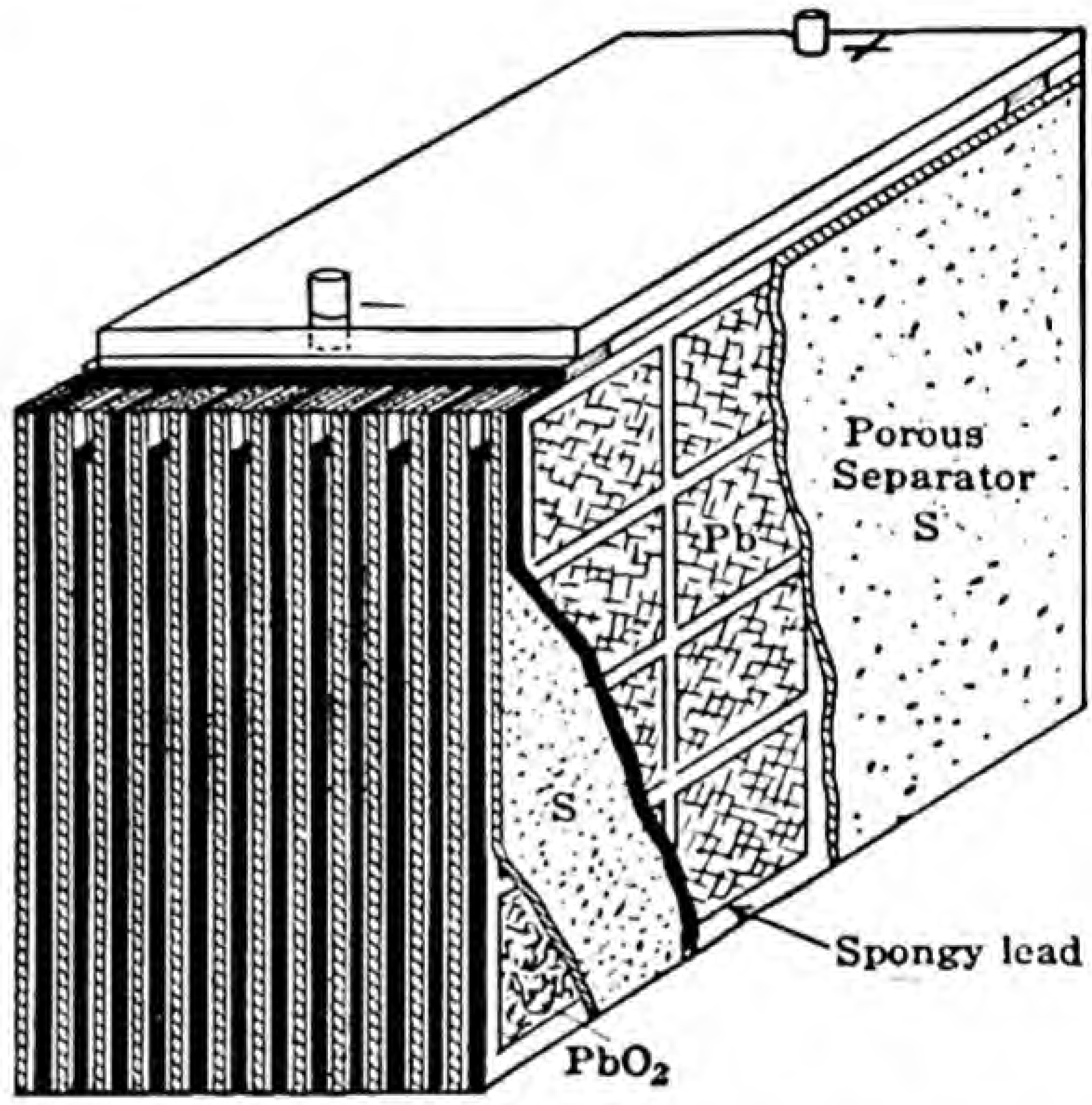


FIG. 164. The lead accumulator or storage cell.

$$\textit{Lead plate:}\quad Pb + SO_4^{--} \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} PbSO_4\text{ (solid)} + 2e$$

$$\textit{Dioxide plate:}\quad PbO_2 + SO_4^{--} + 4H_3O^+ + 2e \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftarrows}} PbSO_4\text{ (solid)} + 6H_2O$$

During discharge, the lead plate is being *oxidized* to lead sulfate, hence serves as *anode;* whereas the lead dioxide plate is being *reduced* to lead sulfate, hence serves as *cathode.* In charging, precisely the reverse reactions take place, the sulfate-covered dioxide plate serving as *anode* and the sulfate-covered lead plate as *cathode.* (Ex. 13.)

The cell just described has an electromotive force of 2.2 volts when

fully charged, decreasing to about 1.9 volts during discharge. The density of the solution meanwhile falls off, owing to the withdrawal of sulfuric acid from the solution, in forming lead sulfate. When the density has fallen to about 1.05 the cell should be recharged. (Ex. 14.)

The *current* that can be drawn from a cell depends on the effective area of the plates. The more expensive of two automobile storage batteries usually has a larger number of plates, joined in *parallel* to give a greater total area, hence a greater storage capacity, in *ampere-hours*. The *electromotive force* is determined by the chemical reaction that takes place in the cell, and is the same for a fully charged small cell as for a large one. Small storage cells in test tubes are sometimes linked together in *series* (p. 615), in research laboratories, to form a battery of several thousand volts, with elaborate precautions to secure good insulation and to prevent fatal accidents from the incautious approach to such a harmless-looking piece of equipment as a shelf full of test tubes.

515. The Edison Storage Cell

Many attempts have been made to produce a light storage cell by substituting some other metal for lead. Most successful is the Edison cell. The *anode*, during discharge, is spongy iron and the *cathode* a rod of nickel surrounded by nickelic oxide, NiO_2. The electrolyte is a 20 per cent solution of potassium hydroxide.

When the cell is discharging, iron is oxidized at the anode, and the nickelic oxide reduced at the cathode. Charging the cell reverses these reactions:

$$Fe + 2OH^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Fe(OH)_2 + 2e$$

$$NiO_2 + 2H_2O + 2e \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Ni(OH)_2 + 2OH^-$$

This cell has an electromotive force of only about 1.2 volts when fully charged, but is very light in weight and may be short-circuited or left idle for long periods without being injured. Such treatment would ruin a lead accumulator.

This seems an appropriate place to remark that the signs + and −, stamped on electrical equipment, are the result of three conventions:

1. The terminals of a *storage battery* are stamped with the signs, + or −, that they have *during discharge*. The anode plate is marked −, since electrons are there freed, during discharge; the dioxide plate is marked +, since electrons there disappear.

2. The terminal of a *generator* from which electrons are forced into the circuit is marked −, and the terminal to which electrons return is marked +. Electrons always move through a circuit from − to +.

3. The terminals of *measuring instruments* are stamped with the signs of the terminals of the source of current (generator or battery) to which they are to be connected. Connect the + of an ammeter or voltmeter with the + of a generator or battery.

516. Couples

We have referred (§ 504) to the increased rate of corrosion of metals whenever the metallic surface happens to be interrupted by impurities occupying a lower position in the electrochemical series than the metal itself. Specks of carbon in the surface of zinc or of slag in the surface of iron or steel furnish a good example. The metal, with its surface impurities, forms a *couple* or short-circuited electrochemical cell. Hydrogen is liberated at the surface of the impurity, which serves as cathode, and surrounding areas of metal become anode and are rapidly corroded. We may avoid this action by amalgamating the surface of zinc (§ 511). On the contrary, we may decrease the rate at which the metals react with acids by deliberately placing them in contact with a more active metal. (Ex. 15.)

517. Speeds of Ions

We have learned that an electric current in a metallic conductor is carried by mobile *electrons*, whereas one in a non-metallic or *electrolytic conductor* (a solution, or a molten salt or alkali) is carried by *ions*, those of opposite charges moving through the solution in opposite directions.

When a current passes through a solution or molten electrolyte all the ions that are present move toward the electrodes and so help to carry the current, but only certain kinds of ions take part in the reactions that always occur at the electrodes (oxidation at the anode and reduction at the cathode). In brief, certain ions migrate toward the electrodes and linger in the neighborhood of the electrodes without being discharged, whereas others are formed or discharged at the surface of the electrodes, either more rapidly or less rapidly than they arrive by migration.

The passage of a current through a solution or molten electrolyte is therefore always accompanied, not only by *electrolysis at the electrodes*, but also by *changes in concentration in the neighborhood of the electrodes*. For example, we may find that metallic copper is being deposited on the cathode, from a solution of copper sulfate, much more rapidly than

copper ions move toward the cathode from distant parts of the solution. The solution around the cathode therefore steadily decreases in concentration.

From the *total changes in concentration* near the electrodes, in comparison with those that would be produced solely by the reactions taking place at the surface of the electrodes, it is possible to calculate *the relative speeds of different sorts of ions, toward or away from the electrodes.* Speeds of the ions (often termed *ionic mobilities*) may also be directly observed, in some instances, from the movement of a visible boundary [3] between two solutions containing different sets of ions. Figure 165 shows one arrangement for maintaining a sharp boundary between solutions of two different salts. The lower solution is continuously formed as cadmium or some other metal dissolves at the anode.

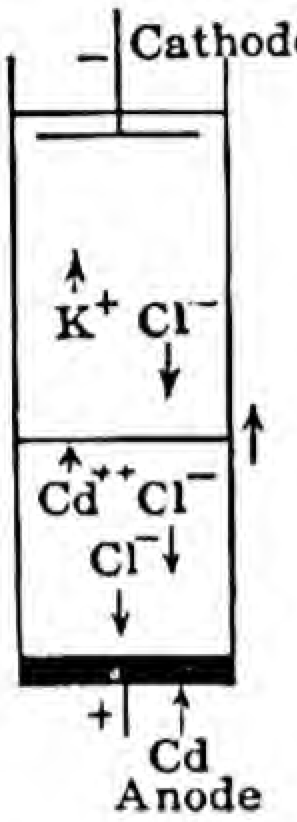


FIG. 165.

The speeds of the ions in a solution are proportional to the potential gradient—the number of volts difference in potential for each centimeter of distance between the electrodes.[4] Speeds of a few ions, for unit potential gradient, are here tabulated:

SPEEDS OF A FEW IONS IN DILUTE AQUEOUS SOLUTIONS AT 18°C

Speeds in centimeters per second when the potential gradient is 1 volt for each centimeter of distance between the electrodes.

Cations		*Anions*	
H_3O^+	33×10^{-4}	OH^-	18.2×10^{-4}
Li^+	3.5×10^{-4}	Cl^-	6.85×10^{-4}
Na^+	4.6×10^{-4}	Br^-	7.0×10^{-4}
K^+	6.75×10^{-4}	I^-	6.95×10^{-4}
Ag^+	5.7×10^{-4}	NO_3^-	6.5×10^{-4}
NH_4^+	6.7×10^{-4}	SO_4^{--}	7.1×10^{-4}
Zn^{++}	4.8×10^{-4}	CO_3^{--}	6.2×10^{-4}

Our table shows that even the most swiftly moving ion (H_3O^+) moves quite slowly. If the potential gradient between the two electrodes is 10 volts per centimeter the speed of this ion in pure water at 18°C is $10 \times (33 \times 10^{-4}) = 0.033$ cm per sec. To traverse 1 cm distance will require about 30 sec. The electrical impulse that sets

[3] Made visible by a difference in color between the two solutions, or by sharp refraction of light at the boundary, owing to a change in refractive index.

[4] This is true only for moderate potential gradients. With very high potential gradients ions have less than their expected mobility.

the ions in motion nevertheless travels with the speed of light. (Ex. 16.)

As the temperature of a solution is increased its viscosity decreases and its ions tend to lose a part of the water of hydration which they must otherwise carry with them. For this reason the ions all move more rapidly and the resistance of a solution *decreases* with increasing temperature. The resistance of a metallic conductor, by contrast, usually *increases* (§ 493) with increasing temperature.

518. Accounting for the High Speeds of Ions from the Solvent

In solutions of acids and alkalies in water, a large part of the current is carried by oxonium ion, H_3O^+, and by hydroxyl ion, OH^-, respectively; for H_3O^+ moves at 5 to 10 times the speed of other univalent cations, and OH^- at about 3 times the speed of other univalent anions (see table on the preceding page). In other words, *in solutions in which water is a solvent, the most rapidly moving ions are the two kinds of ions that are furnished by water itself.*

We can probably explain the high speed of ions furnished by water by recalling that water tends to become associated into complex groups of molecules (§ 123). When a H_3O^+ or OH^- ion, moving through water under the influence of an electric field, collides with one of these complex groups it may be added to the group; but in so doing it may initiate a nearly instantaneous rearrangement of electrons within the group, which causes another H_3O^+ or OH^- ion to be ejected on the opposite side of the group. This is as if the original ion had been able to skip over some of the intervening distance. If this explanation holds, the excess mobility of H_3O^+ and OH^-, in comparison with other ions, should tend to disappear at high temperatures, at which the complex groups of solvent molecules tend to be broken down; and $NH_4{}^+$ and $NH_2{}^-$ should be the most swiftly moving ions in liquid ammonia. These anticipations are fulfilled.

519. Conductance of Solutions

The conductance of a solution (always specified for one contained between parallel electrodes, 1 cm apart) depends (1) on the *number of ions* that the solution contains in each cubic centimeter, (2) on the *charges* that the ions carry, and (3) on the *speed* with which they move. Diluting a solution of a slightly active acid or base causes it to be more completely ionized; but the number of ions *per cubic centimeter* is decreased, hence the conductance of the solution also decreases (often being roughly proportional to the square root of the concentration).

When a solution is heated its viscosity is lowered, hence the ions present in it move more rapidly and its conductance is increased (or its resistance diminished).

Solid salts are ordinarily very poor conductors of electricity, up to temperatures at which they melt or are about to melt. Then they suddenly become good conductors as crystal structure breaks down, in the act of melting, and the ions become free to move.

520. Electrode Products

(Review § 260.)

The reaction taking place at the **anode,** during electrolysis of a solution or a molten salt or alkali, frequently depends on the nature of the anode itself:

1. If the anode is an oxidizable metal (one above gold in the electrochemical series) it will usually be oxidized (will lose electrons), *in a neutral or acid solution*, and will pass into solution as metallic ions:

$$\underset{\text{Metallic copper}}{Cu} \rightarrow \underset{\text{A cupric salt}}{Cu^{++}} + 2e$$

In an alkaline solution, certain metals (especially iron and nickel) usually fail to dissolve when made anode, if any considerable current is passed. Presumably they are protected by an invisible coating of oxide. They are then said to have become "passive" (§ 504).

2. If an "insoluble" (difficultly oxidizable) anode is used (such as graphite, gold, or platinum) the anode product is usually oxygen; but if a chloride or bromide, in sufficiently high concentration, or an iodide, even in a dilute solution, is present the anode product will usually be the free halogen.

The reaction taking place at the **cathode** may usually be predicted from the electrochemical series:

1. Metals nearest the bottom of the series (§ 267) are those whose ions most readily accept electrons and are deposited in metallic form on the cathode:

$$\underset{\text{A silver salt}}{Ag^{+}} + e \rightarrow \underset{\text{Metallic silver}}{Ag}$$

If the ions of several such metals are present it is often possible to deposit them on the cathode, one after another, beginning with the metal that is nearest the bottom of the electrochemical series. For example, a current sent through a solution containing Cd^{++}, Cu^{++}, and Ag^{+} will first deposit silver on the cathode. Then on increasing the

applied electromotive force metallic copper will be deposited; then at a still higher electromotive force even the cadmium will be separated. In this way the different metals present in an alloy can often be separated, when a sample of the alloy has been dissolved in an acid.

2. All the metals occupying positions below aluminum may be deposited on the cathode as just described; but when a metal occupies a position above hydrogen some hydrogen gas is usually produced as well:

$$2H_3O^+ + 2e \rightarrow 2H_2O + H_2\uparrow$$

This is particularly likely to happen if the solution is strongly acid.

3. Metals occupying positions from aluminum upward cannot be deposited at the cathode from *aqueous solutions*, but only from fused salts or alkalies, or occasionally from non-aqueous solutions. The cathode product in the electrolysis of aqueous solutions of compounds of these metals is hydrogen gas rather than the metal.

521. Overvoltage

We have just said that even metals above hydrogen in the electrochemical series may be electrodeposited at the cathode from aqueous solutions, provided they lie below aluminum. This may seem surprising. One might be inclined to say that the cathode product would always be hydrogen gas (from the water) rather than cadmium, zinc, iron, etc., since hydrogen occupies a lower position in the series than any of these metals. The explanation is simple:

1. The position assigned hydrogen (or any other element) in the series is that which it occupies in a solution of unit effective concentration (1 gram ion per liter). For the hydrogen ion this corresponds very nearly to a normal solution of an active acid. As the concentration of any ion is decreased it becomes more and more difficult to discharge that ion—as if the element concerned were being moved upward in the electrochemical series!

So, as a solution is made less and less acid, and at length alkaline, the position of hydrogen is moved upward in the series, finally to about the level of zinc (in alkaline solutions). This in itself would make possible the electrodeposition of all metals below zinc, at least from neutral or alkaline aqueous solutions.

2. The position assigned every element in the electrochemical series is that which it occupies if the gain or loss of electrons at the electrode is *freely reversible* and *instantly accomplished*. Processes that need time for their accomplishment require the expenditure of *extra energy*, which is measured by what is called the *overvoltage* at that particular

electrode. *Overvoltage measures the total effect of all influences that impede or retard a reaction that would otherwise take place freely.*

The need for expending extra energy when hydrogen gas is set free on the surface of certain metals is the chief reason why hydrogen fails to be evolved at the cathode in many cases in which we should otherwise expect it. On zinc, for example, hydrogen has a high overvoltage. So in passing an electric current through an aqueous solution of a zinc salt, even in a somewhat acid solution, the chief cathode product is not hydrogen but metallic zinc.

The following table shows that the overvoltage of a gas at an electrode increases as the current density (in amperes per square decimeter of electrode surface) is increased. The table also shows that hydrogen has the highest overvoltage at the surface of metals like mercury, aluminum, and zinc, in which hydrogen does not dissolve appreciably. The electrode then soon becomes covered with a film of hydrogen, which impedes the passage of the current.

But when an electrode of gold or platinum has been coated with platinum black (in which hydrogen dissolves freely, being dissociated into monatomic hydrogen) the overvoltage, with very small currents, approximates zero. This is just another way of saying that the reaction at the electrode is then instantly accomplished and freely reversible (hence the use of platinum black in a hydrogen electrode, § 402).

TABLE OF OVERVOLTAGES

Hydrogen (*In M* H_2SO_4)

Cathode	*Current Density (Amperes per Square Centimeter)* 0.01	0.1	1.0
Pt (black)	0.03	0.04	0.05
Pt (bright)	0.07	0.29	0.68
Au	0.39	0.59	0.80
Fe	0.56	0.82	1.29
Cu	0.58	0.80	1.25
Pb	1.09	1.18	1.26
Zn	0.75	1.06	1.23
Ni	0.74	1.05	1.24
Cd	1.13	1.22	1.25
Hg	0.93	1.03	1.07
C	0.70	0.89	1.17
Ag	0.76	0.98	1.10
Al	0.83	1.00	1.29

Oxygen (*In M* KOH)

Anode	*Current Density (Amperes per Square Centimeter)* 0.01	0.1	1.0
Graphite	0.52	1.09	1.24
Au	0.67	1.24	1.68
Cu	0.42	0.66	0.84
Ag	0.58	0.98	1.14
Pt (smooth)	0.72	1.28	1.38
Pt (black)	0.40	0.64	0.79
Ni	0.35	0.73	0.87

Data from Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, New York, Prentice-Hall, 1938.

When the processes at the electrodes are freely reversible, so that the overvoltage is zero and the energy expended is at a minimum, water may be electrolyzed by application of an electromotive force of 1.218 volts. But the accompanying table of overvoltages shows that the sum of the overvoltages at the two electrodes may easily amount to 2 volts. To electrolyze water under such conditions requires a total electromotive force of over 3 volts.

High overvoltages are always encountered when an electrode becomes covered with an insoluble film that delays or impedes the access of gaseous or dissolved reactants to the electrode or the removal of reaction products from the electrode.

522. Electroplating and Electrorefining

In electroplating, metallic ions at the cathode accept electrons and are deposited as metallic atoms:

$$M^{++} + 2e \rightarrow M$$

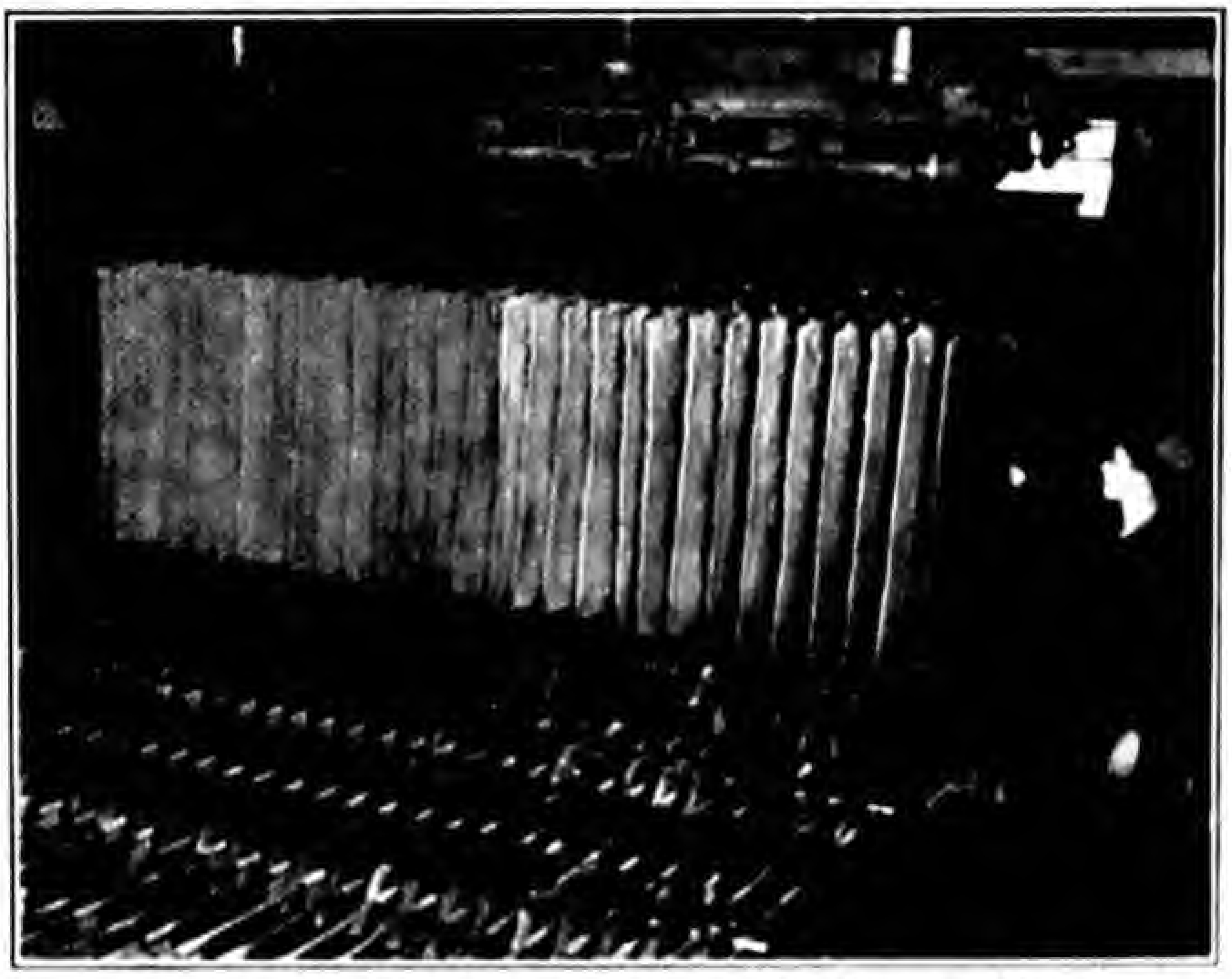
To obtain a smooth deposit that adheres well to the underlying material we must often resort to methods that call for considerable experience and skill. Silver, unfortunately, is deposited by an electric current from a silver nitrate solution in a granular, crystalline form. To get a smooth deposit we must ordinarily use a "cyanide bath," in which most of the silver is in reserve as complex anions, $Ag(CN)_2^-$, in equilibrium at every instant with a very small concentration of Ag^+, continuously being deposited at the cathode.

We may often so reduce the concentration of some ion (by adding something to combine with it, forming a complex ion) that the given metal is deposited only with difficulty. Thus copper may be given a position in the electrochemical series as high as zinc; the two metals then deposit jointly, as brass. Copper and lead may be deposited jointly from a solution containing ammonium sulfate and cupric tetrammine sulfate.

Many metals are purified on a large scale in industry by *electrorefining*—purification by dissolving the metal, then electrodepositing it under conditions that hinder the electrodeposition of impurities. Most of the copper used in industry undergoes such a treatment. Heavy plates of impure copper form the anodes. The cathodes are thin sheets of pure copper; and the electrolyte is a solution of copper sulfate in sulfuric acid (Fig. 166.)

The gold and silver contained as impurities in the anode fail to dissolve, for these metals are much below copper in the electrochemical

series. They accordingly subside as a fine sludge (*anode mud*), which is recovered when the electrolyte is drained from the electrolytic cell. Iron, zinc, and lead, on the other hand, are brought into solution along with the copper; but they fail to be deposited upon the cathode, for they are above copper in the electrochemical series, and have the additional handicap of being present only in small concentration.



Courtesy of Anaconda Copper Mining Co.

FIG. 166. Electrolytic copper refining. Each of the tanks shown in the photograph contains 29 cathodes, arranged alternately with 30 anodes. The crane in the foreground has lifted a set of cathodes for inspection.

Copper is thus continuously dissolved from the anode and redeposited on the cathode. The impurities contained in the anode are removed by something like a double sifting process, gold and silver being got rid of as anode mud, while the more soluble impurities remain in solution, as the copper comes out upon the cathode.

Thirty-two different metals have been electrodeposited but only about half of these are electrodeposited commercially.

523. Faraday's Law

We have seen that the electrochemical series determines *which particular substance* is oxidized at the anode and which one is reduced at the cathode, of all those present. The *quantity* of material transformed at each electrode is determined by *Faraday's Law*, first stated in 1834: (1) *When an electric current is passed through an electrolyte (a solution, or a molten salt or alkali) the quantity of material transformed at each electrode is proportional to the quantity of electricity passed;* (2) *equal quantities of electricity, passed through different electrolytes, transform equal numbers of equivalents of the different elements.*

For example, an *equivalent* (gram-atomic weight, divided by change in valence number) is 107.88 grams for silver, deposited from a solution of any silver salt, Ag^+; 63.57 grams for copper, deposited from a solution of any cuprous salt, Cu^+; and $63.57 \div 2 = 31.785$ grams for copper, deposited from a solution of any cupric salt, Cu^{++}. If equal quantities of electricity are passed through these solutions the quantities of metal deposited on the cathode are proportional to the weights just indicated.

If several different transformations occur together at any electrode (metallic zinc and hydrogen gas, for example, being liberated together at the cathode), we may observe how many equivalents of each product are obtained and so find the total number of equivalents transformed. At the other electrode exactly the same number of equivalents, usually of other materials, will be transformed, in the opposite sense (oxidation occurring at the anode and reduction at the cathode).

Faraday's Law is really a consequence of the fact that *each electron lost or gained produces unit change in the valence or valence number of some particular atom.* To produce unit change in valence or valence number in 1 gram atom of material (6.023×10^{23} atoms) will require 6.023×10^{23} electrons. But each electron carries a charge of 1.602×10^{-19} coulomb of electricity. Altogether, $(6.023 \times 10^{23}) \times (1.602 \times 10^{-19}) = 96{,}500$ coulombs are needed to produce unit change of valence or valence number in 1 gram atom of material. In brief, 96,500 *coulombs transform 1 gram equivalent of material at each electrode.*

The quantity of electricity represented by 6.023×10^{23} electrons or 96,500 coulombs is called a *faraday*. If we pass a faraday of electricity through an electrolytic cell, 1 gram equivalent of material is oxidized at the anode and 1 gram equivalent of something else is reduced at the cathode. Perhaps the simplest way to deal with any instance is to write an electronic equation for the reaction. *For each electron appearing in the equation we need 96,500 coulombs, if the total indicated weight, in grams, is to be transformed.* For example, in the oxidation (anode) of a chromic salt to a chromate, we have

$$Cr^{+3} + 4H_2O \rightarrow CrO_4^{--} + 8H^+ + 3e$$

Three electrons appear in this equation. To produce the indicated weight ($52 + 64 = 116$ grams) of chromate we therefore need $3 \times 96{,}500$ coulombs, provided that this is the only reaction accomplished at the anode. At the same time, three equivalents of something will be reduced at the cathode.

Some Important Electrical Terms

Electrostatic—relating to electricity at rest.

Electromagnetic—relating to electricity in motion, or to the magnetic phenomena that it induces.

Electrostatic unit of charge—a charge that repels (and is repelled by) an equal charge, distant 1 cm, in a vacuum, with a force of 1 dyne. This charge, multiplied by the velocity of light, in centimeters per second (3×10^{10}), gives the **electromagnetic unit of charge** or **quantity** (theoretically, 10 **coulombs**).

Unit charge—in chemistry, the charge on the electron, or an equivalent positive charge. This is 4.8025×10^{-10} electrostatic unit, or 1.602×10^{-19} coulomb. Multiplied by Avogadro's number, it gives the quantity of electricity needed for 1 equivalent of chemical charge (i.e., 1 faraday, or 96,500 coulombs).

Electrical field—any portion of space (for example, an electric circuit) in which electrons or electrically charged material particles (ions) are acted upon by an electrical force. This force sets the electrons or other charged particles in motion or maintains them in motion in spite of their dissipation of energy (as heat) by collision with other particles. In the absence of such collisions (for example, in an X-ray tube) the force due to the field continuously accelerates the moving charges.

Field strength (at a given point in the field)—the force, in dynes, with which an electric field acts upon an electrostatic unit of positive charge.

Potential (electrical)—a measure of the *energy* that must be supplied by some outside agency in moving a unit positive charge (or, frequently, in moving 1 coulomb) against the opposition of an electric field, from some reference point to any specified point in the field. The electrical potential at any point in the field is always increased by increasing the positive charge or by decreasing the negative charge at that point.

Difference of potential (between any two points in a circuit or field)—a measure of the energy that is expended when a unit positive charge (or, frequently, 1 coulomb) moves from a point of higher to a point of lower potential—or when a unit negative charge (or 1 coulomb) moves in the opposite direction.

Electromotive force—a measure of the energy delivered or work done by any current-inducing process, for each unit of charge (in practice, each coulomb) transferred (§ 510). It is not actually a *force*, since force is a measure of energy or work done for each unit of distance traversed (p. 72).

Electrothermics—the use of an electric current as a source of heat. This contrasts with applications in which the primary purpose is electrolysis.

Joule, p. 596. **Watt**, p. 597. **Coulomb**, p. 597. **Ampere**, p. 597.

Milliampere—a thousandth of an ampere.

Coulometer—any instrument for measuring quantity of electricity, in coulombs. In the silver or copper coulometer the quantity of electricity passed is inferred from the weight of metal deposited on the cathode; less accurately, one may note the combined volume of hydrogen and oxygen set free at both electrodes, in the electrolysis of dilute sulfuric acid.

Ammeter—any instrument for measuring an electric current, in amperes.

Milliammeter, wattmeter (left for the student to define).

Kilowatt-hour—the quantity of energy expended in 1 hour by a current that expends energy at the rate of 1000 watts. It is 3.6×10^6 joules.

Ampere-hour—the quantity of electricity transferred by a current of 1 ampere, during 1 hour. It is 3600 coulombs.

Volt—the potential difference or electromotive force that yields a joule of work for each coulomb of electricity transferred through a circuit.

Resistance (electrical)—the ratio of applied electromotive force to current flowing, when a steady current dissipates all its energy as heat.

Resistivity or **specific resistance**—resistance measured between opposite faces of a centimeter cube.

Ohm—the resistance of a circuit in which an electromotive force of 1 volt maintains a steady current of 1 ampere, dissipating all its energy as heat.

Mho (reciprocal ohm)—the conductance corresponding to a resistance of 1 ohm.

Electrochemical cell—any device in which a chemical reaction produces an electric current; or, conversely, one in which a current induces a chemical reaction.

Electrolysis, p. 64. **Primary cell,** p. 601. **Concentration cell,** p. 600.

Secondary cell, p. 601. **Couple,** p. 605. **Electrolytic conductor,** p. 605.

Electrolyte—a solution, or a molten salt or alkali, forming the conducting fluid of an electrochemical cell. The term electrolyte is also used in a less desirable sense, to mean *any ionic substance.*

Polarization, p. 601. **Depolarizer,** p. 601.

Series connection—connecting the + terminal of one electrochemical cell with the − terminal of the next, thus linking the cells to form a **battery** having an electromotive force equal to the sum of those produced by the cells individually.

Parallel connection—connecting all the + terminals of a set of electrochemical cells together, and all the − terminals together. The battery thus obtained has the electromotive force of a single cell, but can deliver as many coulombs as all the cells, taken separately.

Standard electrode potential—the potential of an electrode in contact with a solution in which dissolved reactants are present in unit activity and reactant gases are under 1 atmosphere of effective pressure, when the reaction is electrochemically reversible. The standard potential of a reversible hydrogen electrode is usually taken as zero, and other potentials given in comparison with it. The term **normal electrode potential,** sometimes used with the same meaning, should be avoided, since it may convey the impression that the electrode is in contact with a normal solution.

Current density—the number of amperes of current passing through a unit area (usually 1 sq cm) of an electrode or conductor.

Overvoltage, p. 609. **Electrorefining,** p. 611. **Faraday,** p. 613.

Electron volt, p. 709. **Dielectric constant,** p. 348.

Magnetic permeability—the ratio of the intensity of magnetization induced in a material to the intensity of the magnetic field inducing it. Magnetic permeability is usually represented by μ (mu). It is unity for a vacuum.

Exercises

1. Write electronic equations for the reactions taking place at the anode and cathode of the Weston standard cell, assuming that cadmium dissolves to form cadmium ions at one electrode and that mercurous ions, Hg_2^{++}, are reduced to metallic mercury at the other. Make a sketch to show the direction in which electrons are transferred through the outer circuit. Which electrode is cathode and which is anode?

2. During the discharge of a lead storage cell each atom of lead oxidized at the

anode releases how many electrons? Then how many electrons and how many coulombs of electricity will the cell deliver while 1 gram atom (6×10^{23} actual atoms) of lead is being oxidized? 1.2×, 193

3. Certain types of brass are rapidly corroded by sea water, zinc being dissolved, leaving behind a spongy mass of nearly pure copper. Explain why the zinc is more readily attacked than the copper and why the corrosion, once started, usually progresses very rapidly.

4. A solution contains dissolved salts of copper, cadmium, zinc, and silver. Indicate the order in which these metals will be plated out at the cathode, if the potential applied to the cell is gradually increased.

5. What product would you expect to obtain at each electrode in each of the following cases, and why:

(*a*) Dilute sulfuric acid, electrolyzed between platinum electrodes.
(*b*) Sodium bromide, electrolyzed between graphite electrodes.
(*c*) Sodium hydroxide, electrolyzed between iron electrodes.
(*d*) Cupric sulfate, electrolyzed between copper electrodes.
(*e*) Zinc sulfate, electrolyzed between graphite electrodes.

6. Write electronic reactions for the joint deposition of zinc and copper at the cathode in brass plating. Which metal must be present in very low concentration to prevent it from depositing before the other metal begins to be deposited?

7. What is the current density (amperes/cm^2) at the electrodes when 2.5 amperes pass between parallel graphite electrodes, each 5 cm square? Refer to the table in the text to determine the overvoltage at the cathode, if hydrogen there separates from a sulfuric acid solution. 100, 890

8. Explain how antimony, present as an impurity, will behave in electrorefining copper.

9. How many equivalents in 1 gram atom of iron deposited from a ferric solution? How many in 1 gram atom deposited from a ferrous solution?

10. How long will it take a current of 1 ampere to deposit 1 gram of copper from a cupric solution? 304

11. What actual number of equivalents is represented by 22.4 liters of hydrogen gas? 200

12. How long will it take a current of 1 ampere to liberate 1 liter of hydrogen gas, under standard conditions? 861

13. What actual weight of chromate ion, CrO_4^{--}, in grams, corresponds to a gram equivalent when the chromate is produced by oxidation of Cr^{+3}? 387

14. What current is needed to deposit 1 gram of nickel in 1 hour, from a solution of a Ni^{++} salt? 915

15. In a cell for electrorefining copper, 1000 amperes of current are passed, under a difference of potential of 0.5 volt. What weight of copper is deposited at the cathode in 1 hour, and what energy in kilowatt-hours is expended in doing it? (1 kilowatt-hour = 1000 watt-hours = 3.6×10^6 joules.) 119, 500

16. Cells for the production of electrolytic chlorine take 1000 amperes. How many kilograms of chlorine should be produced in 24 hours? 317

Chapter 38

THE LIGHT METALS

524. General Characteristics of the Light Metals

The light metals include the *alkali metals* (column 1A of the Periodic Table), the *alkaline-earth metals* (column 2A), and *aluminum* (sometimes classed with the heavy metals).[1] Their chemical properties are largely determined by the fact that their atoms readily lose one or two electrons (a share in three electrons, for aluminum), thus producing cations that have the same electronic structure as the next preceding inert gas (§ 238). The most important characteristic of this structure is a *stable outer group of eight electrons*, the possession of which tends to make the light-metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+; Be^{++}, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Ra^{++}) resistant toward oxidation and reduction.

In consequence, it is only by the expenditure of considerable energy, usually delivered by an *electric current*, that the light-metal cations may be compelled to accept electrons and so be converted into the free metals. For this reason the light metals remained undiscovered during many centuries in which primitive man made use of gold, silver, copper, and iron, and civilized man became familiar with still other heavy metals. They were first brought to light by the electrochemical experiments of Davy, in 1807.

Some other consequences follow from this tendency of the light metals to lose electrons and pass over into the ionic state. Very striking is the fact that *their oxides react with water to form alkalies*, which are nearly all *active bases*. The explanation is simple. The loss of electrons by the light metals, and their transfer to oxygen, produce oxides that are *ionic compounds*. When such an oxide is in contact with water the metallic ions become hydrated (combine with water, § 288); but the oxide ion, by virtue of its double charge and small

[1] Aluminum, though of low density, resembles the heavy metals in its chemical behavior.

radius, is able to attract a proton so strongly as to remove it from water:

$$\overset{\curvearrowleft H^+}{O^{--}} + HOH \rightarrow 2OH^-$$
$$\text{(Base)} \qquad \text{(Acid)}$$

The oxides of the heavy metals and non-metals do not thus react, because their oxygen is linked to the other elements in covalent union.

In the reaction just considered the oxide ion acts as a proton acceptor, namely, as a *base*, in the most general sense. The hydroxyl ions, produced by the reaction, must therefore be less "basic" than the original oxide ion. Nevertheless hydroxyl ion is still an active base, as we recognize by its ability to react with acids, capturing a proton:

$$\underset{\text{(From acid)}}{H^+} + \underset{\substack{\text{Hydroxyl ion} \\ \text{(Alkali)}}}{OH^-} \rightarrow H_2O$$

The ability of the light-metal hydroxides to change the color of indicators is explained in the same way. An indicator is merely an acid (or a base) that happens to change color when it loses (or gains) a proton (§ 406).

From the charges and relative sizes of the light-metal cations we can predict something about the solubility of their salts. The cations of the *alkali metals*, for example, are only singly charged, and (except for Li^+) are all of rather large size. They therefore form weak crystals, which are readily torn down in the process of hydrating the ions. In consequence, the compounds of the alkali metals are in general readily soluble. Important exceptions are $LiOH$, Li_2CO_3, Li_3PO_4, which possess not only a very small cation but also a very small or doubly or triply charged anion, and consequently tend to form stronger crystals, only sparingly soluble in water.

The cations of the *alkaline-earth metals*, by contrast, are small in size and doubly charged. They therefore tend to form insoluble compounds, particularly when the anion is doubly or triply charged. Conspicuous exceptions are beryllium sulfate and magnesium sulfate, which are readily soluble (in contrast with the very slightly soluble sulfates of calcium, strontium, and barium). This proves that the tendency toward increased lattice strength, with decreasing cation radius, is sometimes more than offset by an increased tendency toward hydration or by a change to a geometrical structure that is inherently weak. (Ex. 1–6.)

SUMMARY OF PROPERTIES OF LIGHT METALS

1. They readily lose electrons (§ 238).
2. They react with non-metals to form salts that are typical ionic compounds.
3. Their cations have the electronic configuration of the inert gases.
4. They are so reactive that they are never found free in nature.
5. So much energy is needed to separate them from their compounds that they are nearly always prepared by electrolysis.
6. Their oxides react with water to form hydroxides that are active bases (alkalies).
7. Their uni-univalent compounds are usually soluble; their bi-bivalent compounds are usually insoluble.

THE ALKALI METALS

525. Preparation and Uses of the Alkali Metals

1A	
At. no. 3	Li
11	Na
19	K
37	Rb
55	Cs
87	?

Sodium and potassium were first obtained in metallic form by electrolysis of the fused caustic alkalies (sodium hydroxide and potassium hydroxide). Metallic *sodium* is now usually produced by electrolysis of fused sodium chloride (containing a little calcium chloride to lower the melting point). The Downs process is shown in cross section in Fig. 167. The cathode is a strip of iron or copper, surrounding a graphite anode. A diaphragm of iron gauze, interposed between anode and cathode, prevents the products of electrolysis (sodium at the cathode and chlorine at the anode) from coming into contact with each other.

Molten sodium, thus produced, overflows into the container. It usually contains about 3 per cent of calcium; but on cooling to about 150°C solid calcium separates, and may be strained off (the two metals being nearly immiscible in the solid state, since their atoms differ greatly in radius and contain unequal numbers of valence electrons, § 239).

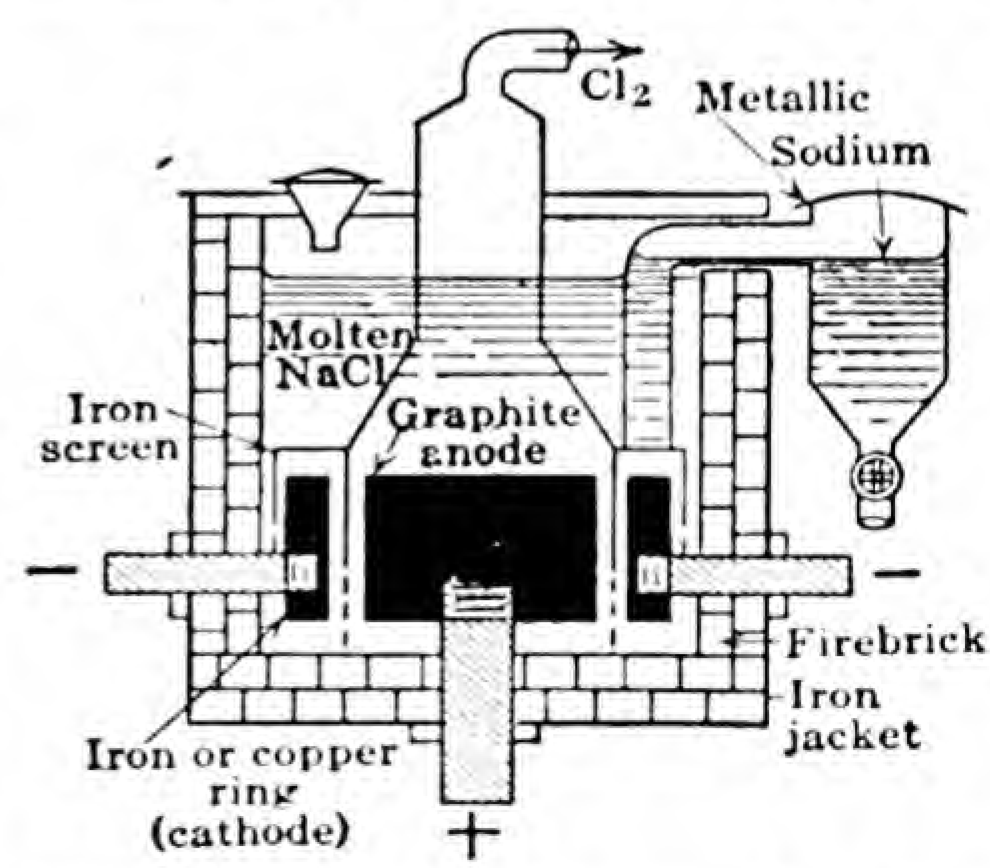


FIG. 167. The Downs cell for preparation of metallic sodium by electrolysis.

Metallic sodium is chiefly used in the preparation of sodium peroxide. The sodium is slowly oxidized in a current of air, at a temperature of about 200° to 400°C. Oxidation of sodium by a limited amount of oxygen or by oxygen under diminished pressure results in sodium monoxide, Na_2O. This is a powerful

absorbent for water and carbon dioxide (being thus converted into sodium hydroxide and sodium carbonate).

An important recent use of metallic sodium is in sodium-vapor lamps, now widely used for highway illumination (Fig. 168).

Metallic *potassium* is commonly made by electrolysis of fused potassium hydroxide, because its tendency to react with iron at high

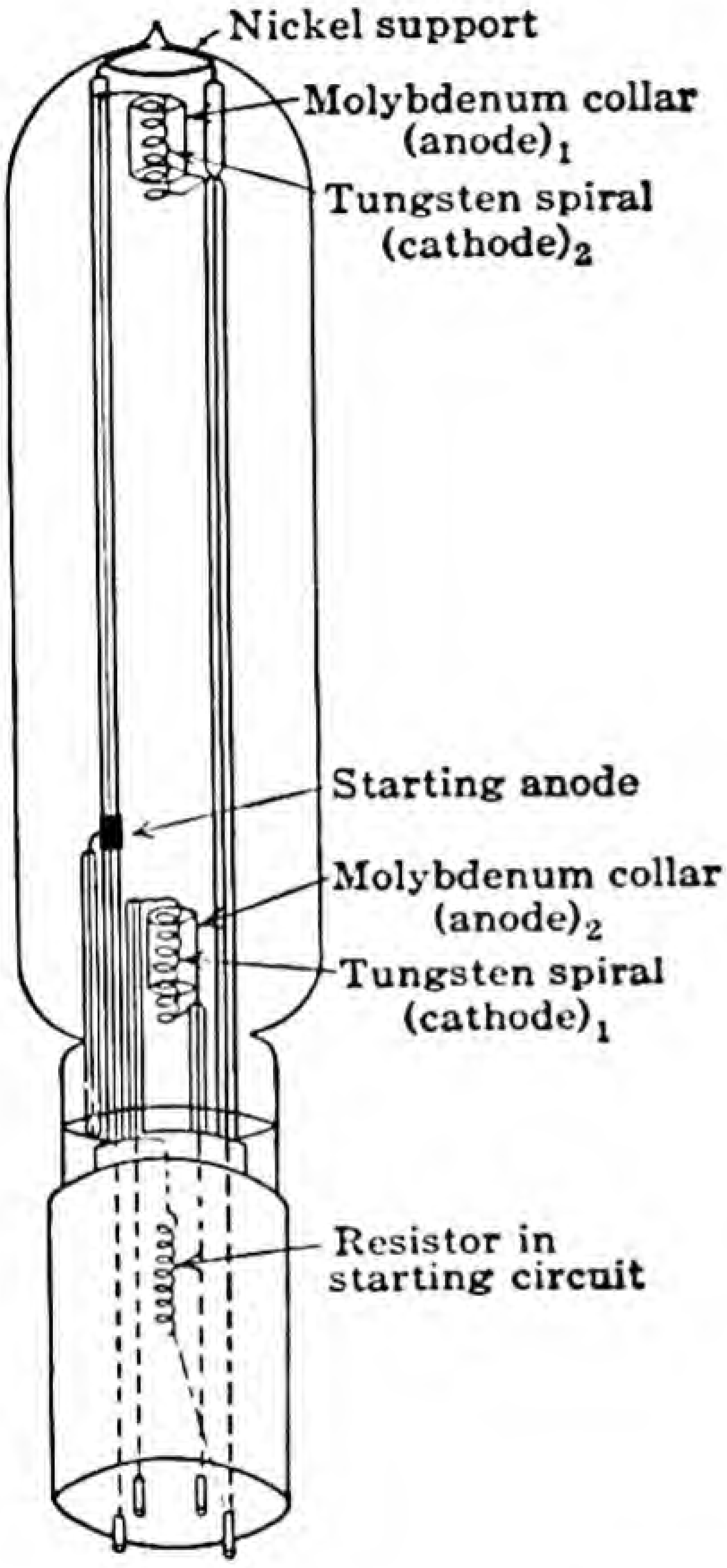


FIG. 168. Sodium-vapor lamp. The lamp is started with the aid of an auxiliary anode, placed near one of the spiral cathodes. The current is carried at first by ions produced by the passage of cathode-emitted electrons through neon gas, contained in the tube under a few millimeters pressure. The tube is contained in a vacuum jacketed flask, not shown in the cut. As it warms up, metallic sodium, contained within the tube, is vaporized, then ionized by the electronic discharge. The current is then chiefly carried by ions produced from the sodium vapor. Subscripts 1 and 2 refer to the successive half-cycles of the 110-volt alternating current. The yellow light is emitted in consequence of electrons within excited sodium atoms reverting to a lower energy level.

temperatures introduces difficulty in its production from fused potassium chloride. It has no important uses for which sodium will not serve as well.

Metallic *cesium* is often used in photoelectric cells. Owing to the ease with which its atoms emit electrons it will respond even to the low-frequency radiant energy of the visible spectrum.

526. Industries Based on Common Salt

Common salt, NaCl, has been used since prehistoric times in such widely different industries as preserving fish, tanning hides, dyeing textiles, and producing a glaze on pottery and other ceramic products. In addition, it serves as raw material in important chemical industries:

1. By treatment with concentrated sulfuric acid, common salt is converted into *sodium sulfate* (raw material for the production of glass)

and *hydrochloric acid* (the source of the chlorides of most of the heavy metals).

2. Electrolysis of a solution of common salt produces chlorine and sodium hydroxide or sodium hypochlorite.

3. By any one of several processes, common salt may be converted into *sodium acid carbonate* or *sodium carbonate*, from which most of the sodium salts used in the chemical industries are prepared.

4. Electrolysis of molten salt yields *metallic sodium* (§ 525), from which *sodium peroxide* is prepared.

5. Fusion of common salt with carbon and calcium cyanamide yields *sodium cyanide* (§ 450), from which the cyanides of other metals and the ferrocyanides are prepared.

527. Industries Based on Sodium Carbonate

Most of the vast quantity of sodium carbonate used in industry today is made by the *Solvay* or *ammonia-soda process* in which common salt, in a saturated solution, reacts with carbon dioxide and ammonia, to give a precipitate of sodium acid carbonate:

$$NaCl + \underbrace{NH_3 + H_2O + CO_2}_{\text{Equivalent to } NH_4HCO_3} \rightarrow NaHCO_3 \downarrow + NH_4Cl$$

By filtering off the sodium acid carbonate, thus obtained, then strongly heating it, the normal salt is obtained:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 \uparrow + H_2O$$

The ammonium chloride that is produced as a by-product of this process is treated with calcium hydroxide to produce ammonia, which is used over again. The final by-product is therefore calcium chloride.

About three fourths of the million tons of sodium carbonate produced in the United States each year (1938) is used in the manufacture of *glass*, other *sodium compounds*, and *soap*. Considerable quantities are used in *water softening* (§ 534).

Potassium carbonate, formerly extracted from wood ashes, is usually made by electrolysis of a solution of potassium chloride, the anode solution (potassium hydroxide) being treated with carbon dioxide. It is used in the production of liquid (soft) soap and in certain varieties of hard glass.

528. The Caustic Alkalies

Sodium and potassium hydroxides are known as *caustic alkalies* or *lye*. They are extremely soluble, deliquescent white solids, prepared commercially (1) by treating a solution of sodium or potassium car-

bonate with slaked lime, $Ca(OH)_2$; or (2) by electrolysis of a solution of sodium chloride or potassium chloride (§ 198).

The most important uses of caustic soda, NaOH, are (1) *in neutralizing acids* (such as a slight residue of acid in petroleum that has been refined by treatment with concentrated sulfuric acid, then washed with water); (2) the manufacture of *rayon* (§ 466); (3) preparation of *paper pulp;* (4) manufacture of *soap;* (5) manufacture of *sodium compounds,* such as the hypochlorite, chlorate, and nitrite. Such uses consume several hundred thousand tons of sodium hydroxide each year and a smaller quantity of potassium hydroxide. A mixture of solid sodium hydroxide and solid calcium oxide is called *soda-lime.* It is used in the laboratory as an absorbent for carbon dioxide.

The Alkaline-Earth Metals

529. Preparation and Uses of the Alkaline-Earth Metals

	2A
At. no.	4 Be
	12 Mg
	20 Ca
	38 Sr
	56 Ba
	88 Ra

Beryllium is easily prepared by the electrolysis of a mixture of beryllium chloride and beryllium fluoride. It is very light, strong, and easily worked, and is sufficiently abundant to be worth considering as a component of light alloys.

Magnesium is made by electrolysis of magnesium oxide, dissolved in fused magnesium fluoride, containing a little sodium fluoride and barium fluoride to lower the melting point. Magnesium is the lightest of the rigid metals of good mechanical strength and reasonably low cost. Though very reactive it is resistant to corrosion under ordinary atmospheric conditions, since it soon becomes covered with a protective film, presumably a hydroxy-carbonate.

Magnesium is an important *reagent* in the synthesis of a number of perfumes and medicinal products. It is a useful *deoxidizer* for nickel and other metals. It forms a number of strong, *light alloys,* now widely used in the production of struts, crankcases, and motor parts for airplanes and speedboats, and in other applications where strength needs to be combined with light weight. Though powdered magnesium burns so readily that it is used in *flashlight powders,* nevertheless massive pieces of the metal may be heated in a forge and then shaped by hammering or rolling, without igniting.

Metallic *calcium* is usually prepared by the electrolysis of molten calcium chloride. It has been used for deoxidizing nickel, aluminum, and magnesium. When added in small amounts to lead, it gives an

alloy that is much tougher and stronger than pure lead. Calcium has been used in removing the last traces of water from *absolute* (100 per cent) *alcohol.* Its ability to combine with both nitrogen and oxygen makes it useful for removing traces of air from apparatus that needs to be maintained at a high vacuum.

Metallic *barium* is most easily obtained by reduction of a mixture of barium oxide and barium peroxide, using aluminum as the reducing agent. The metallic barium so produced is meanwhile separated from the other product, aluminum oxide, by being distilled off in a vacuum at about 1000°C, the vapors being condensed on a water-cooled surface.

530. Hydrides of the Light Metals

All the light metals, with the exception of magnesium and beryllium, combine directly with hydrogen to form hydrides (KH, CaH_2, etc.) in which hydrogen exists as the negatively charged *hydride ion*, H^-. The *alkaline-earth metals* combine with hydrogen so vigorously that they actually burn with a visible flame in an atmosphere of hydrogen. The union with the *alkali metals* is less vigorous, unless the hydrogen reacts under pressure or the metal is very finely divided or present as a vapor.

Sodium hydride, NaH, is a white solid with the crystal structure of common salt. When it is melted and electrolyzed, hydrogen is evolved at the anode, just as chlorine is in the electrolysis of molten common salt. So we are entitled to regard hydrogen, in the light metal hydrides, as playing the part of a *halogen.* In the reaction $H \rightarrow H^+ + e$, by contrast, that is, in yielding electrons, hydrogen plays the part of an *alkali metal.* Its position below all the other alkali metals in the electrochemical series is a consequence of the fact that its very small radius enables it to retain its electron very strongly.

The light-metal hydrides react vigorously with water, forming a metallic hydroxide and liberating hydrogen. They often ignite spontaneously in moist air, and are such vigorous reducing agents that they will even reduce carbon dioxide to carbon. Their salt-like character (they are typical ionic compounds) may be contrasted with hydrides of the transition metals which are interstitial compounds (§ 499), and with the hydrides of the semi-metals (Sb, Bi, Te) and non-metals (As, S, Cl), which are volatile molecular compounds.

531. Calcium Carbonate

Calcium carbonate occurs in inexhaustible quantities in all parts of the world as chalk and limestone. *Chalk, limestone,* and *coral* have

been deposited as the remains of living organisms, ranging from those that are microscopic to shellfish of considerable size. Limestone is harder and more compact than chalk, but still very imperfectly crystallized. *Marble* is more nearly completely recrystallized, and large crystals of pure calcium carbonate, in two distinct crystal forms (*calcite* and *aragonite*), are frequently encountered.

Marble and limestone not only are quarried for building material but also are the raw materials for important chemical industries—the production of quicklime, mortar, and portland cement. In preparing quicklime nearly pure limestone or marble is strongly heated, carbon dioxide being set free.

$$\underset{\substack{\text{Calcium}\\\text{carbonate}\\\text{(limestone)}}}{CaCO_3} \rightarrow \underset{\substack{\text{Calcium}\\\text{oxide}\\\text{(quicklime)}}}{CaO} + CO_2\uparrow$$

The escaping carbon dioxide sets up a definite *dissociation pressure* at each temperature. This pressure increases very rapidly with increasing temperature, as shown in Fig. 169, and equals the pressure of the atmosphere at about 900°C. The escaping carbon dioxide is then able to force back the atmosphere bodily, hence decomposition becomes very rapid. Nevertheless *there is no very definite decomposition temperature for calcium carbonate.* It is gradually decomposed at a much lower temperature than 900°C, at a rate which is limited by that at which the escaping carbon dioxide is carried away by diffusion or by the rate at which the ions within the crystal move over from the positions they occupy in the $CaCO_3$ lattice to those they are to have in the CaO lattice.

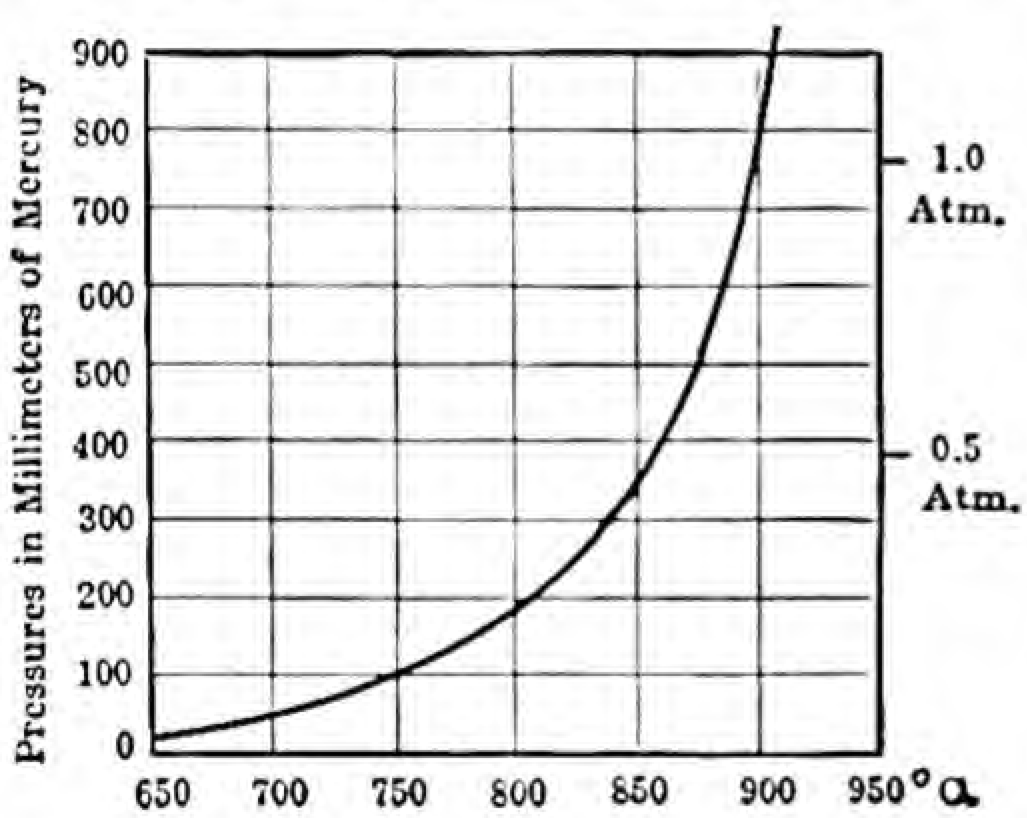


FIG. 169. Dissociation pressure of calcium carbonate.

The decomposition of calcium carbonate begins at the corners and edges of the crystals and gradually extends through the whole crystal structure. *Decomposition may be stopped and reversed at any time, and the original crystal reconstructed, by exposing the partially decomposed crystal to carbon dioxide, under a pressure greater than the dissociation pressure of calcium carbonate at that temperature.*

Carbonates of the other alkaline-earth metals and those of the heavy metals are similarly decomposed by heat. This proves that the

carbonate ion, CO_3^{--}, is somewhat unstable, owing to the mutual repulsion of its three oxygen atoms, which are closely packed about a small central atom of carbon (Fig. 170). In the carbonates of the alkali metals (Na_2CO_3, for example) the presence of two univalent cations of comparatively large size almost completely blocks the escape of carbon dioxide from the crystal lattice, except at very high temperatures. Sodium carbonate is accordingly only very slightly decomposed by being heated to redness for an hour or more.

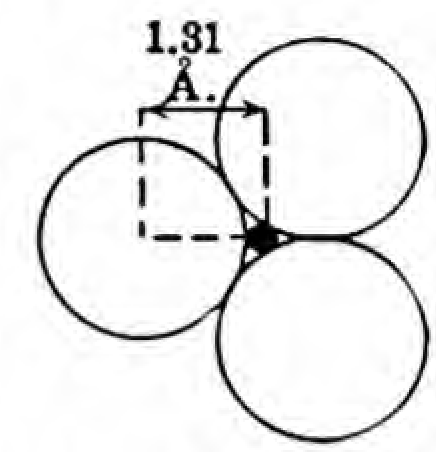


FIG. 170. The CO_3^{--} ion.

532. Carbonates and Acid Carbonates

To understand what comes next in our discussion of the industries based on calcium carbonate we must pause for a glimpse of the chemistry of the *carbonates*, in comparison with the *acid carbonates:* The carbonates of the *alkaline-earth metals* are all insoluble, since the mutual attraction of oppositely charged *doubly charged* ions, within the crystal lattice, produces a lattice that is too strong to be disrupted by the tendency of the ions, when in contact with water, to become hydrated.

Among carbonates of the *alkali metals* only lithium carbonate is slightly soluble, as already explained (§ 524). All the other alkali metal carbonates (Na_2CO_3, K_2CO_3, etc.) are readily soluble, the solubility increasing rapidly with increasing ionic radius, and reaching a maximum with rubidium carbonate.

On the addition of an acid, in small concentration, to an insoluble carbonate, protons are transferred from the acid to carbonate ions at the surface of the crystal:

$$\underset{\text{From acid}}{H^+} + \underset{\text{Carbonate ion}}{CO_3^{--}} \rightarrow \underset{\text{Acid carbonate ion}}{HCO_3^-}$$

By thus diminishing the charge on the anion the crystal structure is weakened and the crystal dissolves. It is for this reason that calcium carbonate has its solubility *increased* about thirtyfold, by conversion into acid carbonate, with even so weak an acid as carbonic acid. On the contrary, sodium or potassium carbonate is already fairly soluble. Its solubility is somewhat *decreased* by conversion into acid carbonate, owing to the formation of hydrogen bonds (§ 272) between the carbonate ions, thus somewhat increasing the strength of the crystal.

If we add an acid, in any very high concentration, to either a soluble or an insoluble carbonate or acid carbonate, a second proton is captured. The energy thus released disrupts the carbonate ion, freeing carbon dioxide:

$$2H^+ + CO_3^{--} \rightarrow \underset{\text{Carbonic acid}}{H_2CO_3} \rightleftharpoons H_2O + CO_2\uparrow$$

533. Calcium and Magnesium Salts in Water Supplies

Water percolating through the soil usually carries enough dissolved carbon dioxide (perhaps chiefly present as carbonic acid) to dissolve considerable quantities of calcium carbonate.

$$CaCO_3 + H_2CO_3 \rightarrow \underset{\text{Calcium acid carbonate}}{Ca(HCO_3)_2}$$

If water containing calcium acid carbonate, dissolved in this way, is heated, the reaction just formulated is reversed, carbon dioxide escapes, and calcium carbonate is precipitated as a scale on the walls of the kettle or boiler. When ground water containing dissolved calcium acid carbonate drips through the roof of a cave, the release of pressure permits some of the dissolved carbon dioxide to escape and calcium carbonate is precipitated, gradually building up deposits that may become columns, reaching from roof to ceiling.

Water that contains dissolved calcium acid carbonate, precipitable by boiling, is said to have *carbonate* or *temporary hardness*.

Water is said to possess *non-carbonate* or *permanent hardness* (hardness not precipitable by boiling) when it contains dissolved magnesium or calcium salts other than the acid carbonate. The salts chiefly responsible for permanent hardness are calcium and magnesium chloride and sulfate, with perhaps traces of ferrous or ferric salts and manganese salts.

Hard water is not injurious to health but is objectionable in steam engineering practice, since it tends to deposit scale in the tubes of preheaters and boilers. This scale interferes with the transfer of heat from furnace gases through the walls of the tubes into the water. In extreme instances it may lead to overheating of the boiler tubes and a consequent explosion. Furthermore, hard water wastes soap by precipitating it as insoluble calcium and magnesium soaps. It frequently contains traces of iron and manganese salts, which may stain fabrics.

534. Water Softening

Water may be softened—freed from salts responsible for hardness—by adding borax, water-glass, or trisodium phosphate, to precipitate calcium and magnesium as insoluble salts. Such procedures are usually limited to small-scale applications, as in the household.

On a larger scale, in industry, or for filling locomotive boilers, water is usually softened by precipitating magnesium by the addition of *slaked lime*, then calcium by the addition of *sodium carbonate:*

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH_2)\downarrow + CaSO_4$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$$

The precipitate is permitted to settle, then the softened water is siphoned off.

Water is also frequently softened by being filtered through an artificial or natural *zeolite* (a silicate mineral distinguished by its extraordinary porosity, § 484). The bivalent calcium and magnesium ions are strongly adsorbed on the surface of the mineral, displacing sodium ions. After the zeolite (trade-names: Refinite, Permutite) has taken up a considerable quantity of calcium and magnesium ions, these may be displaced and the zeolite *regenerated* by passing strong brine through the softener:

$$\underset{\text{Zeolite}}{Na_2Z} + \underset{\substack{\text{(In hard}\\ \text{water)}}}{CaCl_2} \underset{\textit{Regenerating}}{\overset{\textit{Softening}}{\rightleftharpoons}} CaZ + 2NaCl$$

By using saturated brine, sodium ion is given a high enough concentration to enable it to displace calcium ion from the used zeolite, in spite of the extra tendency of the calcium ion to be held fast, owing to its double charge and smaller size.

Water softeners have also been prepared from which calcium and magnesium salts displace protons rather than sodium ions. They are regenerated by treating them with dilute acids, then washing them.

The term zeolite is now often extended to organic products that resemble mineral zeolites in being capable of cation exchange. When lignite or soft coal is treated with sulfuric acid or chlorosulfonic acid, $SO_2(OH)Cl$, a product is obtained that is capable of exchanging protons, H^+, for the cations of a salt solution. If hard water is filtered through a bed of such material—often called a "carbonaceous zeolite"—not only Ca^{++} and Mg^{++} but also Na^+ are exchanged for H^+, released by the zeolite. The operation of course demands acid-resistant equipment, such as wood, rubber-lined steel, or "stoneware." When

the zeolite has become inactive it is regenerated by treatment with dilute (0.5 to 4 per cent) sulfuric acid. Water treated as just described is both soft and free from sodium salts, but has acquired an equivalent amount of acid. If this is carbonic acid it may be removed as carbon dioxide by passing the water through a deaerating heater.

Certain synthetic resins also purify water by removing active or fairly active acids by acid adsorption. A combined treatment (proton exchange, then acid adsorption, then perhaps aeration) will produce water that is as pure as most distilled water. It has been used to remove inorganic salts from molasses, thus permitting the recovery of a further amount of sugar from the molasses. It has also been used for purifying water for the preparation of solutions of medicinal products—indeed for all applications that otherwise would call for the relatively expensive purification of water by distillation.

535. Mortars and Cements

When calcium oxide (*quicklime*) comes in contact with water a violent reaction occurs, liberating considerable heat and forming calcium hydroxide (*slaked lime*):

$$CaO + H_2O \rightarrow Ca(OH)_2 + 84.4 \text{ kilocal}$$

This reaction, of course, is the result of the fact that both the ions of calcium oxide have a strong tendency to combine with or react with water (§ 524). Calcium hydroxide is only slightly soluble (about 1.85 grams in each liter, at 0°C).

When a suspension of calcium hydroxide is mixed with sand the result is *mortar*, used since prehistoric times for setting bricks or stones in a wall. The setting of mortar is the result of a reaction with the carbon dioxide of the atmosphere:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Minute crystals of calcium carbonate, thus produced, bind the particles of sand together into a coherent mass.

The setting of mortar is, of course, greatly retarded in locations to which the carbon dioxide of the air does not readily penetrate. Within the masonry of castle walls, erected during the Middle Ages, mortar has sometimes been found to be still incompletely hardened. That is why considerable importance is attached to the discovery, long ago, of several kinds of *hydraulic cements*, so called because of their ability to set under water, or when the carbon dioxide of the air is completely excluded. Most important was the cement developed in Roman

times. It was made by strongly heating volcanic tuff—a soft stone found in the environs of the city of Rome—a little lime often being added, previous to heating. The product was ground to a fine powder, then mixed with sand and water to produce a strong hydraulic cement.

We now understand that Roman cement depended on the fact that the volcanic tuff consisted of finely divided siliceous material (volcanic ash), intermingled with clay and chalk. Heating this mixture brought about a chemical reaction in which calcium aluminosilicates (§ 537) were produced. Setting consisted of the formation of crystals of hydrated aluminosilicates, which interlocked with the particles of sand, thus binding the material into a solid mass.

Magnesia cement (*Sorel cement*) is produced by mixing powdered light magnesium oxide [2] with some inert material, such as sawdust, kaolin, or pumice. When mixed with a strong solution of magnesium chloride the cement sets by a reaction that forms magnesium hydroxide, intermingled with a hydrated magnesium hydroxychloride. Cements of this type are light, strong, and resistant to heat, but are easily damaged by water.

Plaster of paris is made by heating gypsum, $CaSO_4 \cdot 2H_2O$, until about three fourths of its water of hydration is expelled. The finely divided product sets by rehydrating, forming a mass of interlocking crystals of gypsum. *Keene's cement* is made by strongly heating gypsum until it is completely dehydrated, then incorporating a little alum, which catalyzes the rehydration.

Stucco is sometimes portland cement and sometimes a gypsum cement, intermingled with sand and, often, wood fiber.

Dental cements, in imitation of porcelain, usually contain a porous, reactive form of calcium silicate, mixed with zinc oxide, and wet with a solution of phosphoric acid. They set by hydration of the phosphate-silicate mixture. Cements for temporary fillings are often made by mixing zinc oxide with a solution of zinc chloride. They set in the same manner as magnesia cements, just described.

536. The Manufacture of Portland Cement

Modern cement is produced by intermingling of raw materials rich in lime (CaO) with other materials rich in alumina (Al_2O_3) and silica

[2] The light or fluffy form of magnesium oxide is made by decomposing magnesium carbonate, at temperatures below about 800°C. The escape of carbon dioxide from the crystal lattice leaves the residue of magnesium oxide in an extremely porous condition. On being heated to above 1000°C this residue shrinks to about one-fourth its original bulk, correspondingly increasing in density.

(SiO_2). The *lime* is commonly furnished by limestone of a rather inferior grade, carrying a few per cent of impurities; or in some cases by chalk or marl (a deposit of mixed chalk and clay, dredged from ponds or river bottoms). The *alumina* and *silica* are furnished by clay, shale, slate-rock, or occasionally by blast-furnace slag.

The manufacture of portland cement is carried out in four stages, shown in outline in Fig. 171.

1. The dry materials are finely ground and mixed, in the proportion of about 4 or 5 parts of limestone to 1 of shale or clay. The

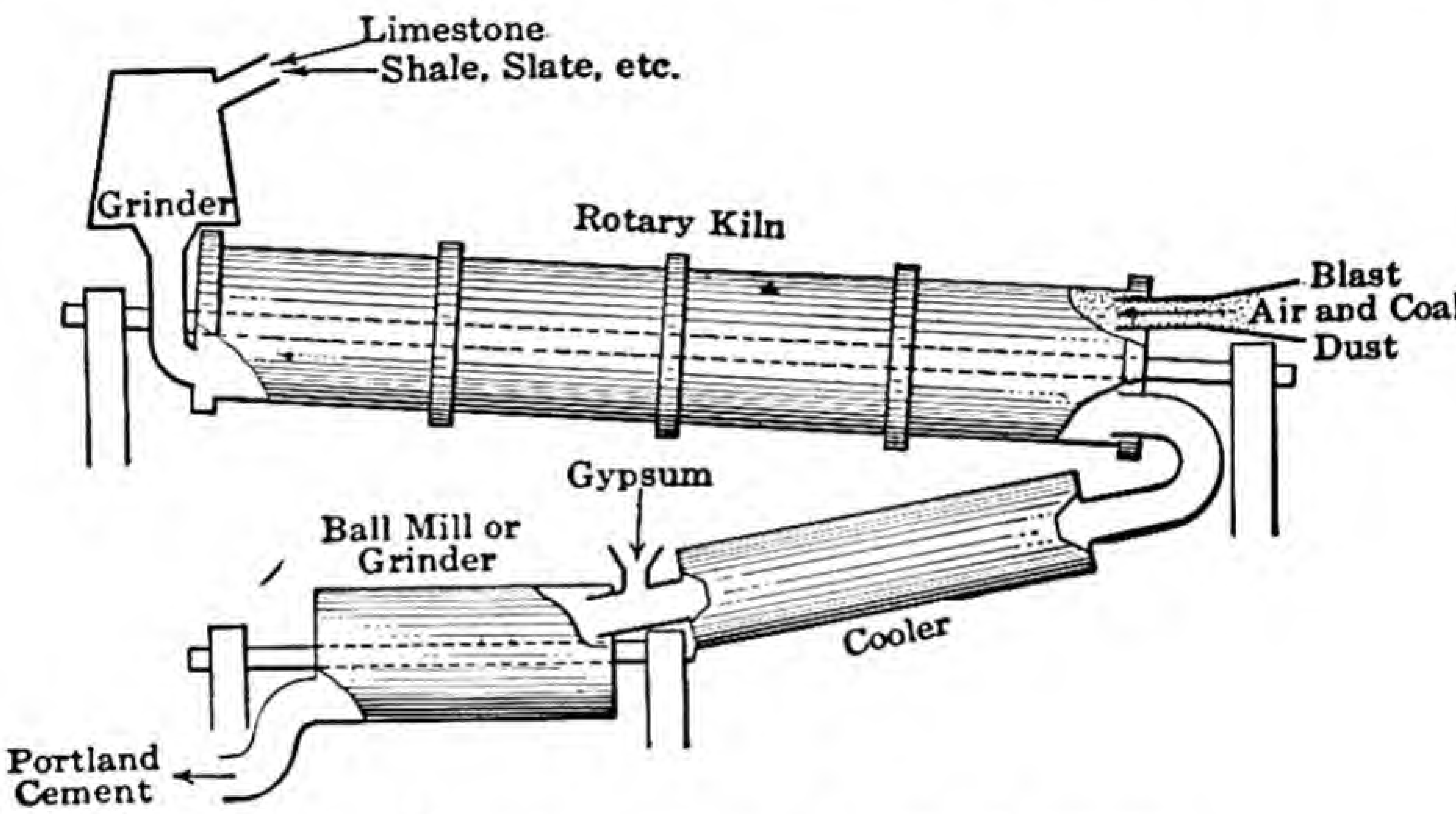


FIG. 171. Preparation of portland cement.

mixing must be very intimate, and in the "wet process" is aided by the addition of enough water to the finely ground material to form a thin paste or "slurry."

2. The wet "slurry" (or the intimate mixture of powdered limestone and clay) is fed into a rotary cement kiln—a revolving inclined tube from 6 to 8 feet in diameter, and 60 to 150 feet long, of sheet steel, lined with firebrick, and fired at its lower end with a blast of air and powdered coal.

The raw material, in passing through the kiln, is dried and calcined, carbon dioxide being expelled from the limestone, leaving calcium oxide. This reacts with the alumina and silica, to form silicates and aluminates, the excess lime being held in solid solution. The product is discharged from the kiln as pellets or balls of greenish-gray clinker, partially fused on the surface.

3. The clinker is cooled by passing through a rotating cylinder, traversed by a current of air. At the same time, it is mixed with about

2 or 3 per cent of gypsum, $CaSO_4 \cdot 2H_2O$, which lengthens the time required for the cement to set.

4. The mixture of clinker and gypsum is ground to an extremely fine powder, in rotating tubes partially filled with steel balls. This is the finished cement.

537. Composition and Setting of Portland Cement

Portland cement contains *an excess of lime and magnesia over silica and alumina.* This places it in sharp contrast with glass, which has an excess of silica, and almost no alumina. A satisfactory cement contains about:

60–64% CaO	2–4% FeO
20–24% SiO_2	2–4% MgO
5–9% Al_2O_3	1–2% SO_3 (present as $CaSO_4$)

Concrete is a mixture of cement with sand and gravel.

The setting of portland cement begins as a process of solution, in which the particles of the finely powdered clinker partially dissolve, the excess of calcium oxide being converted into calcium hydroxide. Crystal growth, accompanied by hydration, begins almost immediately. The water that has been intermingled with the concrete mixture is soon nearly all bound fast in the growing crystals of hydrated calcium aluminosilicates. These soon become large enough to bind the grains of sand and gravel into a coherent solid. The concrete then has its *initial set.*

A slow increase in hardness, over weeks or months, finally takes place, as crystal growth continues and as calcium hydroxide sets to a colloidal gel, which becomes hard and horn-like, as it gradually loses water. This is the *final set.* The strength of the finished concrete, made from good cement, depends chiefly on care in avoiding too much water in making up the original mixture.

Quick-hardening cements are made by fusing limestone with bauxite (hydrated Al_2O_3) in an electric furnace. They usually contain about:

$$42\%\ CaO;\ 42\%\ Al_2O_3;\ 10\%\ Fe_2O_3;\ 5\%\ SiO_2$$

They set by forming a hydrated calcium aluminate, rather than an aluminosilicate, the initial set taking place sufficiently slowly to make the addition of gypsum unnecessary. The final hardening process, by contrast, takes place so rapidly that the same strength may be attained in a single day as is possible with ordinary portland cement in a full month.

538. Compounds of Strontium and Barium

Strontium is fairly widely distributed in nature as the carbonate and sulfate. Strontium hydroxide has sometimes been used in recovering cane sugar from molasses, since it combines with sugar to form a compound that can be separated by crystallization, then decomposed by carbon dioxide, freeing the sugar. Strontium nitrate and other strontium salts are used to produce a red color in fireworks and signal flares.

Barium chiefly occurs as the carbonate and sulfate. The carbonate is decomposed in the same manner as calcium carbonate, though with more difficulty, on being heated:

$$BaCO_3 \underset{(b)}{\overset{(a)}{\rightleftharpoons}} BaO + CO_2$$

Its slow decomposition at high temperatures makes barium carbonate useful as a source of carbon dioxide, in case-hardening steel (§ 562). The decomposition may be accomplished at a much lower temperature if the material is heated in contact with coke, which removes the carbon dioxide as fast as this is formed, by reacting with it to produce carbon monoxide. Thus reaction (*b*), above, is prevented, whereas (*a*) continues and becomes complete (Principle of Mass Action, § 338).

Barium sulfate, heated in the presence of coke, is reduced to barium sulfide. The sulfide and the oxide, produced as just described, react with acids to produce various soluble barium salts. *All soluble barium salts are intensely poisonous.*

Barium carbonate is often added in small quantities to brick and tile, to convert soluble sulfates into insoluble barium sulfate, thus preventing the formation of a white scum or "efflorescence" of soluble sulfate on the surface of the material, when it is exposed to the weather. Barium nitrate and chloride are used to give a green color in fireworks and flares. Barium fluosilicate is an important insecticide for use on fruits and vegetables, and the carbonate is an effective rat poison.

Anhydrous barium perchlorate is an important desiccant (drying agent) [3]—evidence that the configuration of the crystal lattice and the large size of the ions result in a low *lattice energy.* Otherwise expressed, the crystal lattice of barium perchlorate is so readily torn down that the hydration of the ions, in the presence of water, is practically unopposed. The extraordinary solubility of the perchlorate (about 200 grams in 100 grams of water, at 25°C) is a further consequence.

[3] There is grave risk of an explosion in using perchlorates as desiccants, whenever the air being dried contains readily oxidizable vapors.

539. Peroxides

The most interesting and perhaps the most useful barium compound is the peroxide, BaO_2. With the corresponding peroxides of calcium and strontium it illustrates the ready decomposition of the peroxide ion, O_2^{--}. This has the electronic formula $\left[:\ddot{\underset{\cdot\cdot}{O}}:\ddot{\underset{\cdot\cdot}{O}}: \right]^{--}$, which differs from that of oxygen gas in that the two oxygen atoms are connected by a single bond. The center-to-center distance between the atoms is therefore greater (1.31 Å in peroxide ion, as compared with 1.20 Å in gaseous oxygen), and the bond is more readily broken. In consequence, ionic peroxides are readily converted into oxides, on being heated, in a reversible reaction (dissociation) evolving oxygen:

$$\underset{\text{Peroxide ion}}{2O_2^{--}} \rightleftharpoons \underset{\text{Oxide ion}}{2O^{--}} + \underset{\hookrightarrow O_2}{2O}$$

The escaping oxygen, from any given peroxide, sets up a definite pressure at each temperature. This dissociation pressure (§ 531) with barium peroxide reaches 0.21 atmosphere (the partial pressure, § 118, of the oxygen in the atmosphere) at about 725°C; and 1 atmosphere at about 800°C. So if barium oxide is heated in the air to a temperature just below 725°C it rapidly absorbs oxygen from the air and is converted into the peroxide; if the peroxide is heated above 800°C it is rapidly decomposed, reverting to the oxide and evolving pure oxygen, under sufficient pressure to drive back the atmosphere (as in collecting oxygen over water, in a pneumatic trough or gas container). This method is sometimes used as a source of purer oxygen than can be readily obtained from liquid air. (Ex. 7, 8.)

Barium peroxide is used in production of hydrogen peroxide:

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$$

Commonly, an excess of sulfuric acid is used, which is afterward neutralized with powdered barium carbonate. Then on filtering off the precipitate of barium sulfate and unchanged barium carbonate a solution of hydrogen peroxide is obtained. This may be concentrated by distillation in a vacuum. From the concentrated liquid nearly pure crystalline hydrogen peroxide may be obtained by freezing. Solutions of more than a few per cent concentration decompose very rapidly unless protected by traces of an inhibitor, such as acetanilide. Those containing over 90 per cent hydrogen peroxide decompose explosively in contact with various catalysts. But hydrogen peroxide of 40 per cent strength or more can be stored for long periods in aluminum tanks.

Hydrogen peroxide is a covalent compound, which has recently been shown to have the structural formula $\mathrm{H{-}O\diagdown_{O{-}H}}$; but the molecule is twisted about the O—O axis, so that the two hydrogen atoms lie in separate planes, intersecting at about an angle of 100°. The kinked or twisted molecule, in water and hydrogen peroxide, is brought about by the presence of unshared electron pairs (§ 250).

Hydrogen peroxide is an active *oxidizing agent*, especially in alkaline solutions, in which the perhydroxyl ion, OOH^-, doubtless comes into play. But in the presence of readily reducible heavy-metal oxides (such as mercuric oxide, HgO) it also serves as a *reducing agent*, transferring atomic hydrogen to the reducible oxide, and evolving oxygen gas:

$$H_2O_2 = 2H \text{ (transferred to oxide)} + O_2\uparrow$$

$$2H + HgO \rightarrow Hg + H_2O$$

Hydrogen peroxide, in contact with the enzyme *catalase*, present in the blood, is rapidly decomposed, evolving oxygen. Finely divided platinum also decomposes it, apparently by adsorbing monatomic hydrogen from the H_2O_2 molecule, then handing on this hydrogen to a second molecule, which is thereby reduced to water:

$$H_2O_2 \rightarrow 2H \text{ (adsorbed)} + O_2\uparrow$$

$$2H + H_2O_2 \rightarrow 2H_2O$$

Hydrogen peroxide may be viewed as a very weak acid, from which the light-metal peroxides, which contain the anion O_2^{--}, are derived. Such compounds as PbO_2 and MnO_2 are not peroxides but *dioxides*, as is evidenced by the fact that they fail to form hydrogen peroxide when they are treated with acids. They are apparently covalent compounds, in which the two oxygen atoms are more intimately associated with the metal atom than they are with each other. *Organic peroxides* appear to be rather directly related to hydrogen peroxide, one or both the hydrogen atoms of hydrogen peroxide being replaced by organic radicals. (Ex. 9–15.)

Aluminum

540. General Characteristics of Aluminum

Aluminum resembles the light metals, in columns 1A and 2A of the Periodic Table, in several important respects:

1. It is so reactive that it is never found free in nature.

2. So much energy is needed to divorce it from union with oxygen that it is ordinarily prepared by electrolysis, in which all the energy that may be needed can readily be brought to bear, simply by increasing the potential applied to the electrochemical cell.

3. The energy level next below that of the three outer "valence electrons" contains a stable, complete group of 8 electrons (§ 237), instead of an incomplete group of 9 to 16 as with the transition heavy metals, or a group of 18, as with the other heavy metals.

Nevertheless *its tendency to form covalent compounds* and *the tendency of its salts toward hydrolysis* make aluminum seem more like a heavy metal than a light metal, in most of its reactions. In the valence state +3 it resembles chromium, ferric iron, the rare-earth elements, and three rare elements (gallium, indium, and thallium) that fall below aluminum in the Periodic Table. It even has some resemblance to the non-metals boron and silicon, though these have a much greater tendency than aluminum to form volatile molecular compounds, on account of their smaller atomic radius.

541. Preparation and Properties of Metallic Aluminum

The principal aluminum ore is *bauxite*, a hydrated aluminum oxide, approximating the formula $Al_2O_3 \cdot 2H_2O$. This needs to be purified, usually by being dispersed in sodium hydroxide solution, separated from undissolved ferric oxide, then reprecipitated by being agitated with a small portion of previously precipitated material (thus lowering the ratio of alkali to aluminum oxide below the range in which the dispersion is stable).

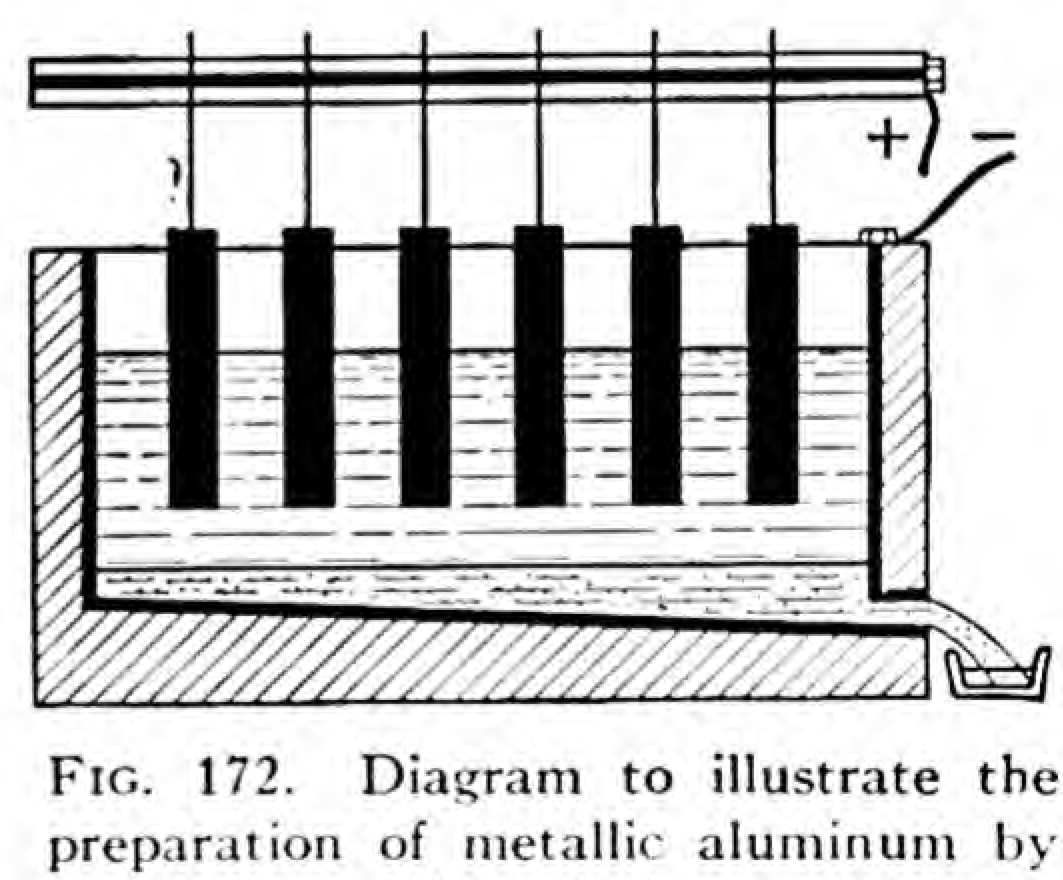


Fig. 172. Diagram to illustrate the preparation of metallic aluminum by electrolysis.

The electrolytic furnace for the production of metallic aluminum consists of an iron box, lined with carbon blocks, which serve as a cathode (Fig. 172). The anode consists of a set of carbon plates, which are lowered from the ceiling by means of a block and tackle. After an arc has been struck, some *cryolite* is thrown in. This is an aluminum mineral, Na_3AlF_6, mined chiefly in Greenland. It melts (1000°C) to a clear, conducting liquid, in which purified anhydrous aluminum oxide is easily dissolved. The flow of current through the cell liberates enough heat to keep the cryolite fused. The aluminum

that is produced collects at the bottom of the furnace, and is tapped out from time to time and cast into bars or ingots.

Aluminum has great tensile strength, is extremely light, and rusts only superficially. When heated to about 100°C, it has considerable malleability, and can be shaped by stamping (milk-cans and bottles). It is easily drawn into wire if alloyed with about 1 per cent each of nickel and copper.

Very pure aluminum is made by an electrolytic refining process, in which a copper-aluminum alloy serves as anode, beneath a bath of molten salts containing fluorides of aluminum, sodium, and barium. The cathode is a layer of pure aluminum, which (in contrast with the copper-alloy anode) is so light that it floats on top of the bath. Pure aluminum has a beautiful silvery luster. It has generally replaced silver in astronomical mirrors. The general experience that very pure metals are resistant to corrosion has been observed again with aluminum. A method has been developed for covering *duralumin* (93.5–95.5 per cent Al, 3.5–5.5 per cent Cu, 0.5 per cent Mn, 0.5 per cent Mg) with a thin coating of pure aluminum as a protection against corrosion.

The most important aluminum alloy is *magnalium*, which contains 5 to 30 per cent magnesium. It is tough and strong, and is free from a fault of pure aluminum in that it does not adhere to lathe tools or a file. *Aluminum bronze* (90 per cent Cu, 10 per cent Al) has a beautiful golden luster, is resistant to corrosion, and is stronger than ordinary bronze.

Aluminum powder is widely used as a reducing agent, in the production of other metals (thermite process, § 507).

542. Aluminum Salts

Aluminum chloride, Al_2Cl_6, is a readily volatile molecular compound, prepared by reducing aluminum oxide, at high temperatures, by carbon, in a current of chlorine:

$$Al_2O_3 + 3C + 3Cl_2 \rightarrow Al_2Cl_6 \uparrow + 3CO \uparrow$$

This salt is of considerable importance as a catalyst in the cracking of petroleum (§ 460) and is a widely used reagent in organic synthesis.

Aluminum chloride is readily soluble in water, but any attempt to recover it from an aqueous solution by evaporation results in complete hydrolysis, leaving a residue of hydrous aluminum oxide:

$$Al_2Cl_6 + 6HOH \rightarrow 2Al(OH)_3 + 6HCl \uparrow$$

What really happens is, of course, the replacement of successive chlorine atoms in Al_2Cl_6 by water molecules, which concurrently release protons. The result is a hydroxy-salt (§ 399) dispersed in a solution containing the ions of hydrochloric acid (H_3O^+ and Cl^-). If a solution of aluminum chloride is evaporated in a current of hydrogen chloride gas, hydrolysis is prevented (Mass-Action Principle, § 338) and crystals of a hydrate, $AlCl_3 \cdot 6H_2O$, may be obtained.

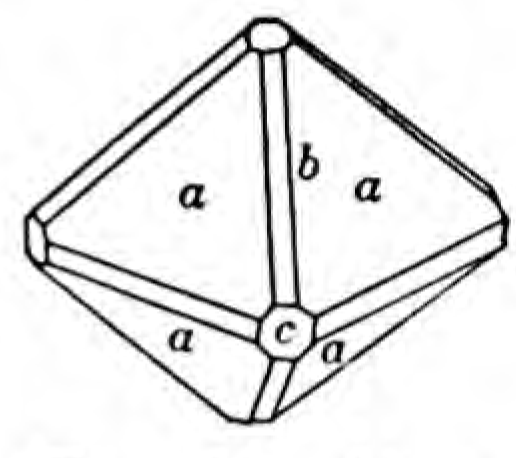


FIG. 173. Alum crystal.

Aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, is used in settling suspended clay in river water intended for municipal water supplies. Its hydrolysis leads to the formation of flocs of gelatinous hydrous oxide, to which bacteria and clay particles tend to cling. Filtration through a bed of sand, followed by chlorination, then aeration, gives water that is safe to drink. Aluminum sulfate is also used in sizing paper and in tanning hides. Its use as a *mordant* in dyeing depends on hydrolysis, which deposits a slightly soluble hydroxy-salt in the fiber. This then combines with the dye.

Ordinary *alum* is a double salt, $KAl(SO_4)_2 \cdot 12H_2O$, having the same general uses as aluminum sulfate. It is an example of the famous series of double salts called *alums*, with the general formula $M^+M^{+3}(SO_4)_2 \cdot 12H_2O$, in which M^+ represents almost any univalent cation (Na^+, K^+, NH_4^+, Tl^+, etc.) and M^{+3} represents almost any tervalent cation (Al^{+3}, Cr^{+3}, Mn^{+3}, Tl^{+3}, etc.).

The alums crystallize in nearly identical crystal forms (Fig. 173), though a progressive slight alteration of the axes of symmetry and crystalline angles, following the order of the elements in the Periodic Table, is detectable with accurate instruments. Over 60 different alums are known. Selenates and some other salts, of corresponding formulas to the alums, and of the same crystal form, have been prepared. It is interesting to observe that lithium, on account of its relatively small ionic radius, apparently does not form alums. (Ex. 16, 17.)

543. The Ceramic Industries

When granite and certain related rocks are exposed to weathering, they are gradually disintegrated, and their more soluble ingredients are dissolved and removed. In the end, all the soda and potash may disappear, leaving a residue of alumina and silica in a hydrated condition. This we call *clay.* The purest clay (*kaolin*) approximates the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, but its composition varies somewhat with

the circumstances under which it is formed. Ordinary clay is, furthermore, almost always intermingled with undecomposed fragments of the original rock, such as flakes of mica.

Industries making use of clay as their chief raw material are called the ceramic industries, and their products are called ceramic products. These are of three chief classes:

1. *Unglazed porous material:* bricks, pottery, terra cotta.
2. *Porous material, glazed superficially:* earthenware.
3. *Non-porous material:* stoneware, chinaware, porcelain.

Most ceramic products are shaped on a potter's wheel, or are cast, as a thin paste, into a mold of porous material, which absorbs the excess water. Subsequent drying is followed by firing in a kiln at a high temperature. The result is *dehydration*, accompanied by a shrinkage and loss of plasticity on the part of the clay; and eventually an actual *partial fusion* of the more readily melted constituents, forming a fluid which serves to cement the remainder of the material into a solid, stony mass, often without so completely blocking the pores as to make the product entirely impervious to water.

English *chinaware*, or bone china, differs from pottery and resembles porcelain in being completely non-porous. Though it usually receives a coating of glaze or enamel, it is not dependent upon this for imperviousness to water. It is molded from a mixture of bone ash (calcium phosphate), kaolin, and feldspar (about in the proportion 3:2:1). When this material is fired in a kiln, the bone ash and feldspar fuse to a certain extent, and fill up the pores between the particles of kaolin. A surface glaze is applied to improve its appearance and prepare it for decoration in color.

Stoneware is a dense, heavy, non-porous ceramic material, used in the industries for pumps and piping for circulating acids. Its ingredients are refractory clay, with a proportion of fluxing material, such as feldspar, to insure that the pores shall become completely filled with fluid at the unusually high temperature at which the ware is fired. Sometimes a vitreous glaze is applied in addition.

Porcelain is made from kaolin, quartz, and feldspar. These are finely ground, intimately blended, made into a paste, molded, dried, and fired at a low temperature. The objects thus formed are covered with a paste of kaolin, quartz, marble, and feldspar, and fired again. True porcelain is translucent throughout, owing to actual fusion of the feldspar and other fusible components and to the penetration of the fused material into the pores of the unfused kaolin body.

Technical Words

Dissociation pressure—the pressure exerted by the gaseous products formed by dissociation of a solid at any specified temperature. It is also the pressure under which the products of dissociation are in equilibrium with the solid.

Carbonate hardness, p. 626. **Non-carbonate hardness,** p. 626.

Hydraulic cement—any cement that has the property of setting under water, or when carbon dioxide is excluded.

Lattice energy—the energy that must be expended in separating the component particles of a crystal, in vaporizing a gram-formula weight of crystalline material. It is also the decrease in potential energy that occurs as the particles approach one another, in taking up positions in crystal lattice.

Ceramic, p. 638.

Exercises

1. Which of the alkali metals has the lowest ionization potential (§ 238) and why?

2. Which of the alkali metals, when emitting electrons in a photoelectric cell, should respond to light of the lowest frequency (§§ 178, 324), and why?

3. Sulfide ion reacts with water in a similar manner to oxide ion. Hence account for the alkaline reaction of solutions of the light-metal sulfides.

4. Is the tendency of sulfide ion to react as just described conspicuously more or less than the corresponding tendency of the oxide ion? Why?

5. Would the reactions of oxide ion and sulfide ion with water be classed as hydrolysis (§ 397)?

6. Is the order of the light metals in the electrochemical series in general the same as the order of decreasing tendency to lose electrons (as measured by ionization potential or ionization energy)? Which light metal (§ 524) is an exception, and why?

7. What weight of sodium peroxide can be made from a pound of sodium? 170

8. What volume of air, under standard conditions, will furnish the oxygen needed to prepare a kilogram of sodium peroxide? 134

9. Write equations for the reaction of common salt with sulfuric acid, in two stages, the final product being sodium sulfate.

10. Write ionic equations for the reactions at anode and cathode in the electrolysis of a solution of common salt.

How may a hypochlorite be made from the products thus obtained?

11. The ammonium chloride obtained as a by-product in the Solvay process may be reconverted into ammonia by treatment with slaked lime. Write an equation.

What is shown by this equation to be the final by-product of the Solvay process?

12. Assuming a current efficiency of 100 per cent, how many ampere-hours (p. 614) are needed to produce a gram-formula weight of potassium carbonate, by electrolysis of potassium chloride, in presence of carbon dioxide gas? 536

13. Write electronic equations for two successive steps in which hydride ion is converted into a proton. Which of these reactions occurs with the lower expenditure of energy, and why? Where would this fact place hydride ion in the electrochemical series?

14. Write an ionic equation (§ 397) to explain why solutions of the carbonates of the alkali metals react strongly alkaline.

15. A liter of hard water contains 10 mg of Ca^{++} and 2.4 mg of Mg^{++}. How many milligram ions of each ion are present? 250, 100

How many millimoles and what actual weight of $Ca(OH)_2$ are therefore needed to precipitate the Mg^{++}? How many millimoles and what actual weight of Na_2CO_3 must be added to precipitate all the Ca^{++} then present? 100, 740, 350, 371

16. Write an ionic equation to explain (§ 396) what happens when aluminum salts are hydrolyzed. Why does aluminum ion have such a strong tendency toward hydrolysis?

17. Write an equation for the reduction of chromic oxide by aluminum.

Chapter 39

THE TRANSITION METALS

In preceding chapters we have given a glimpse of about thirty-seven elements. Over fifty remain, including nearly all the heavy metals, among which at least iron and copper are vital to civilization of the kind that exists today. For us to dispose of the fifty in the few pages that remain may seem too abrupt an ending. Our purpose was nevertheless not to review a parade of the elements but to disclose principles and points of view. The general characteristics of the heavy metals, *in the metallic state*, surveyed as a group, have been given in Chapter 36. In our study of their *compounds* we may concentrate on a few heavy metals that serve as types for the rest, or that are of particular industrial importance. Their *valence states*, the *types of compounds* that they form, their tendency to form *complex ions*, and their chief *industrial uses* are worthy of notice.

544. Valence States of the Light Transition Elements

The transition elements possess an incomplete inner shell of electrons,[1] which is gradually built up from 9 to 18 electrons, as we pass toward the right in the Periodic Table. Most important are the *light transition elements*, from scandium (atomic number, 21) through nickel (atomic number, 28), summarized in the table on the next page. All these elements possess two electrons in the highest energy level or "outermost shell" (except chromium, which has but one). Less energy is needed to remove these two electrons than to remove those in lower-lying energy levels. The result is a doubly charged cation.

The divalent cations of the transition metals all show a tendency to yield a third electron or a share in the control of a third electron. They consequently serve as *powerful reducing agents*, the product being a covalent compound with the valence number +3.

We observe a gradual transition in the *tervalent state:* Ti^{+3} is a vigorous reducing agent, Cr^{+3} is indifferent, Fe^{+3} is a mild oxidizing

[1] Two incomplete inner shells, for the rare-earth elements.

Column	3B	4B	5B	6B	7B	8B		
Atomic number	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni
Electrons in two highest energy levels	9,2	10, 2	11, 2	13, 1	13, 2	14, 2	15, 2	16, 2
Valence Number +2	Sc^{++}	Ti^{++}	V^{++}	Cr^{++}	Mn^{++}	Fe^{++}	Co^{++}	Ni^{++}
+3	Sc^{+3}	Ti^{+3}	V^{+3}	Cr^{+3}		Fe^{+3}	Co^{+3}	
	Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3	Co_2O_3	Ni_2O_3
+4		$TiCl_4$ TiO_2 TiO_3^{--} (Titanates)			MnO_2		CoO_2	NiO_2
+5			V_2O_5 VO_3^{-} (Metavanadates)					
+6				CrO_3 CrO_4^{--} $Cr_2O_7^{-}$	MnO_4^{--} (Manganates)	FeO_4^{--} (Ferrates)		
+7					Mn_2O_7 MnO_4^{-} (Permanganates)			

agent, Co^{+3} is a vigorous oxidizing agent. This is the same as saying that the oxidation potential (which measures the relative tendency of a substance to be oxidized or to serve as a reducing agent, § 267) is positive for the reaction $Ti^{++} \rightarrow Ti^{+3} + e$, and even for $Ti^{+3} \rightarrow Ti^{+4} + e$, but is negative for $Co^{++} \rightarrow Co^{+3} + e$.

In the *quadrivalent state* (+4) four light transition elements form dioxides, which are weak anion-forming oxides ($TiO_2 + O^{--} \rightarrow TiO_3^{--}$). Titanium dioxide, TiO_2, is stable, even when strongly heated, but the other three dioxides (MnO_2, CoO_2, NiO_2) are readily converted into the oxides Mn_3O_4, Co_3O_4, Ni_3O_4 by reducing agents or by being strongly heated. The product, in each instance, may be regarded as a combination of the divalent and tervalent states (since $MnO + Mn_2O_3 \rightarrow Mn_3O_4$).

In the *sexavalent state*, the compounds of chromium (CrO_3, CrO_4^{--}, $Cr_2O_7^{--}$) show more stability than corresponding compounds of manganese and iron. Soluble chromates react slightly alkaline, on account of hydrolysis:

$$CrO_4^{--} + 2H_2O \rightarrow H_2CrO_4 + 2OH^-$$

With the manganates (MnO_4^{--}, green color), tendency toward hydrolysis is stronger yet, manganese dioxide and a permanganate being produced (§ 550). For this reason the manganates are stable

only in alkaline media; and ferrates (FeO_4^{--}, blood-red color) can be obtained only by the action of vigorous oxidizing agents, in alkaline media, and soon revert to the tervalent state.

545. Scandium, Yttrium, and the Rare Earths

3B
21 Sc
39 Yt
57–71 Rare Earths
89 Ac

Scandium and yttrium are frequently included in the rare-earth group, though they differ from the other rare-earth metals in having only one incomplete shell of electrons. Like the other rare-earth elements they are tervalent in all their important compounds.

Because the rare-earth elements differ only in the number of electrons in a deep-lying inner shell they are so nearly alike in their reactions and in the solubility of their salts that they can be separated only with great difficulty. Their separation from one another has frequently been accomplished by a tedious process involving hundreds or thousands of successive fractional recrystallizations. This work has recently been very much assisted by the discovery that several of the rare-earth elements may be obtained in the bivalent condition by the electrolytic reduction of a solution of their tervalent salts. Elements that otherwise would be practically indistinguishable are thus made sufficiently different to be separated.

Monazite (a complex phosphate, found in Brazil and India) is the principal source of the rare-earth elements. Some of the members of the rare-earth group are really very rare, but cerium is available in considerable quantities, and a standard solution of ceric sulfate, $Ce(SO_4)_2$, is an important oxidizing agent.

The 15 rare-earth elements, beginning with lanthanum (No. 57) are sometimes called the *lanthanide elements*. In passing through this sequence, the third outermost shell of electrons is completed, while the other shells remain unaltered.

546. The Actinide Elements (Nos. 89-96)

In the position beneath the rare-earth elements, in the periodic table, is another group of closely related elements, the *actinide elements*.[2] At present, 8 are known. In passing through this group, electrons are again being added to the third outermost group, instead of to the outermost or second outermost group. The atoms of all these elements

[2] In the 18-column table, facing the back cover of this book, the lanthanide elements and actinide elements are separately listed, near the bottom of the table.

are *unstable*, though thorium and uranium decompose with extreme slowness.

Important valence numbers of the actinide group are +3, +4, +5, +6, the lower valence states being the more readily attained and the more stable with the later members of the group.

Actinium is an unstable element of exceedingly brief life, which is produced by the decomposition of atoms of protoactinium. The latter is itself produced by the decomposition of atoms of a rare uranium isotope, ^{235}U.

Thorium is not very abundant, though considerable supplies are available in monazite sand. It is a typical quadrivalent element in all its important compounds. The Welsbach mantle, used to increase the luminosity of the gas flame, is a mixture of the oxides of thorium (99 per cent) and cerium (1 per cent).

Protoactinium is so rare that it was first obtained in weighable quantities in 1927. Subsequently, 5 tons of discarded residues from the production of radium yielded a full half gram of protoactinium in the form of the salt K_2PaF_7. The atomic weight of protoactinium turned out to be 231, which is definitely less than that of the preceding element, thorium.

Uranium won our attention in a previous chapter on account of its radioactivity. The uranium isotopes ^{238}U and ^{239}U are the ancestors of radium and actinium, respectively, in radioactive sequences that finally end with two isotopes of lead (§ 574). Uranium salts are used in the production of uranium glass, which possesses a beautiful, yellowish green fluorescence. Uranium was the first source of atomic energy (details in §§ 591–594).

547. Titanium, Zirconium, and Hafnium

4B
22
Ti
40
Zr
72
Hf

Though *titanium* is commonly classed as "rare," this is only because its separation from other elements is difficult. It is actually the tenth most abundant element in the earth's crust. Its chief ores are the dioxide (*rutile*, TiO_2) and ferrous titanate (*ilmenite*, $FeTiO_3$). The dioxide is widely used as a "permanent white" paint pigment and as a glaze for porcelain. Metallic titanium is used as an alloying element in steel and nickel alloys.

Zirconium occurs as the orthosilicate, $ZrSiO_4$. It is quadrivalent in all its important compounds. It tends toward a non-metallic character in that its halides, such as $ZrCl_4$, are completely hydrolyzed in water, and its most stable compounds are the zirconates (example:

Na_2ZrO_3), which are closely analogous to the silicates. The oxide zirconia, ZrO_2, has been used as an infusible, corrosion-resistant furnace lining.

Zirconium is nearly always accompanied by *hafnium*, discovered in 1923, but so rare that it is still of no industrial importance.

548. Vanadium, Columbium, and Tantalum

Vanadium is best known as the pentoxide V_2O_5, used in catalyst mixtures for the preparation of sulfuric acid by the contact process (§ 315). This oxide reacts with metallic oxides to form stable salts, the metavanadates (containing the ion VO_3^-). Metallic vanadium in steel produces an alloy that is tough and strong, and less weakened at high temperatures than ordinary steel.

5B
23 V
41 Cb
73 Ta
91 Pa

Columbium (formerly called niobium) resembles vanadium in forming only a few stable salts and in being chiefly known in anions, in association with oxygen. This behavior is characteristic of most of the transition metals and is doubtless in some way dependent on the presence of an incomplete inner shell of electrons.

Tantalum occurs as ferrous tantalate, $Fe(TaO_3)_2$. It is treated to remove columbium, which always accompanies it, by fusing the pulverized ore with potassium fluoride. The product, K_2TaF_7, is separated from the columbium salt by fractional crystallization.

From solutions of its soluble salts, tantalum may be obtained as a bright metallic deposit by electrodeposition. It is very strong, ductile, and malleable. *It is remarkably resistant to acids, including even aqua regia*, but is slowly oxidized and dissolved by hot concentrated sulfuric acid. It is occasionally used as a corrosion-resistant plating for precision weights for chemical balances. We have already mentioned the use of tantalum carbide in tools for cutting steel (§ 499)

Tantalum is slowly oxidized when strongly heated in the air. Its tendency toward superficial oxidation permits it to be employed as a current rectifier, when it dips into a solution of dilute sulfuric acid, with lead serving as the other electrode. When the surge of current is in such a direction as to make tantalum the anode, an oxide film is produced, which interrupts the current; when the surge of current is in the opposite direction the oxide film is instantly reduced and the current continues to pass. An electrode of aluminum in an alkaline solution (sodium borate and sodium carbonate), the other electrode being lead or graphite, will also rectify an alternating current, though

less efficiently. Rectifiers of this type have been very largely displaced by vacuum-tube and mercury-arc rectifiers.

549. Chromium, Molybdenum, and Tungsten

The most useful chromium ore is *chromite*, $Fe(CrO_2)_2$, though traces of chromium are found in a great many other minerals and are responsible for the red color of the ruby (essentially, Al_2O_3) as well as the green color of the emerald (a beryllium-aluminum silicate).

Chromium compounds of all valence states are always colored.

Metallic chromium has a brilliant silvery luster and fails to tarnish even in moist air. It is very hard, but brittle. Its chief use, as *ferrochrome* (Fe, 30–40 per cent; Cr, 60–70 per cent; C, 1–8 per cent), is for toughening and hardening steel; but it forms hard alloys (described elsewhere) with nickel, cobalt, and copper. Chromium plating is non-tarnishable, much harder than nickel plating, and adheres better to many surfaces.

Chromates are produced by fusing chromic oxide or chromite ore with an alkali or alkali metal carbonate, in the presence of a vigorous oxidizing agent, such as sodium nitrate or sodium peroxide. *Chromates become dichromates when treated with an acid, and dichromates are reconverted into chromates when treated with an alkali:*

$$\underset{\substack{\text{Chromate}\\(\text{yellow})}}{2CrO_4^{--}} + 2H^+ \rightleftharpoons \underset{\substack{\text{Dichromate}\\(\text{orange})}}{Cr_2O_7^{--}} + H_2O$$

Chromium salts are used in tanning hides into leather. *Chrome yellow* (lead chromate) is an important paint pigment. *Chromic oxide*, Cr_2O_3, is a green pigment, used in coloring chinaware and porcelain. The mineral chromite is sometimes molded into firebricks.

Molybdenum chiefly occurs as lead molybdenate, $PbMoO_4$, and the disulfide *molybdenite*, MoS_2, a black mineral, closely resembling graphite. The metal has a silvery luster and resembles iron in its capacity for being hardened by carbon. Steel containing molybdenum is tough, strong, and resistant to sudden shocks or blows.

6B
24 Cr
42 Mo
74 W
92 U

The most important molybdenum salt is ammonium molybdate, $(NH_4)_2MoO_4$, which is used as a test for phosphates or phosphoric acid, as already described (§ 389).

Tungsten occurs chiefly as insoluble tungstates, $CaWO_4$ and $(Fe,Mn)WO_4$. Metallic tungsten has a higher melting point (3370°C) than any other metal. For this reason, and because of its low volatility, it is used in filaments for electric lamps. Tungsten steel

is indispensable for the production of tools that retain their cutting edge even when heated.

Sodium and ammonium tungstates are often used to make fabrics fire-resistant. Their partial hydrolysis precipitates a hydroxy-salt in the fibers.

550. Manganese, Masurium, and Rhenium (Column 7B)

Manganese occurs in traces in most soils and in the ashes of many plants. The most important manganese mineral is *pyrolusite* or manganese dioxide, MnO_2. Manganese-iron ores can be reduced in a blast furnace under carefully regulated conditions, for the production of *ferromanganese* and *spiegeleisen* (§ 561). High-grade manganese ores are sometimes reduced by carbon in an electric furnace. To prepare the pure metal, free from carbon, it is necessary to resort to the thermite process (§ 507).

Pure manganese is a hard, brittle metal, which resembles iron very closely. It is much more readily oxidized than iron, and is decidedly more reactive.

Manganous salts, Mn^{++}, are oxidized to manganates, MnO_4^{--} (green), by vigorous oxidizing agents, under alkaline conditions, for example, by fusion with a mixture of sodium carbonate and peroxide or nitrate. On dissolving the mixture thus obtained and saturating it with carbon dioxide (to decrease the alkalinity) the manganate is hydrolyzed and in part precipitated:

$$3MnO_4^{--} + 6H_2O \rightleftharpoons 3H_2MnO_4 + 6OH^-$$
$$\hookrightarrow \underset{\text{Permanganic acid}}{2HMnO_4} + MnO_2\downarrow + 2H_2O$$

The precipitated manganese dioxide may be filtered off, and the remaining two thirds of the manganese recovered as a *permanganate*. This is the method by which permanganates are usually prepared, commercially.

Element 43 (masurium) has been prepared artificially, but probably does not exist in nature, because its atoms are unstable.

Element 73 (rhenium) is a very rare relative of manganese whose compounds have nevertheless been well studied. It forms, for example, stable perrhenates, analogous to the permanganates.

551. Ferrous and Ferric Salts (Column 8B)

Ferrous and ferric salts are strikingly different in color (ferrous salts are usually light green and ferric salts yellow to brown). They

are readily convertible, the one into the other, by a large number of oxidizing and reducing agents.

$$Fe^{++} \rightleftharpoons Fe^{+3} + e$$

Ferric salts are much more easily hydrolyzed than ferrous salts. This is evidence that Fe^{+3}, owing to its larger charge and smaller radius, forms stronger bonds that Fe^{++} does with the oxygen atoms of surrounding molecules of water, hence (§ 396) has a greater tendency to release protons:

$$Fe^{+3} + 6H_2O \xrightleftharpoons{\text{Hydrolysis}} \underset{\text{Complex cation}}{Fe(H_2O)_5(OH)^{++}} + \underset{\substack{\text{(Transferred}\\\text{to solvent)}}}{H^+}$$

Ferric salts thus yield *hydroxy-salts* (formerly called basic salts). If the hydrolysis proceeds far enough, the complex cation forms a precipitate, consisting of a complicated insoluble network (§ 399).

552. Cobalt and Nickel

Cobalt usually occurs as an arsenide or sulfide, in association with nickel and other metals. It is a bright silvery metal, with a slight bluish cast. It is not readily tarnished or corroded, but is less abundant than nickel, its nearest rival, and is somewhat less brilliant.

Cobalt is *bivalent* in most of its simple salts. But in the *tervalent* condition it readily coordinates water, ammonia, and a wide range of other substances, forming stable complex ions, in numerous crystalline complex salts. An example is the union of tervalent cobalt, Co^{+3}, with six nitrite ions, to form the cobaltinitrite ion:

$$Co^{+3} + 6NO_2^- \rightarrow Co(NO_2)_6^{---}$$

Observe how the charge on the original cobaltic particle is reversed by its union with the nitrite ions. Sodium cobaltinitrite, $Na_3Co(NO_2)_6$, is an important reagent in testing for potassium ion, the product being a yellow precipitate, $K_2NaCo(NO_2)_6$. Other complex cobalt salts are mentioned in § 557.

Cobalt salts are readily identified by their ability to give a *blue bead* when fused with borax. In solution in water, cobalt salts are *pink*, in sharp contrast with salts of nickel, which are *green*.

Nickel is mined chiefly in Canada, New Caledonia, and northern Finland. In the Canadian ores it is associated with copper, hence it comes on the market chiefly as *Monel metal*—an alloy containing about 2 parts of nickel to 1 of copper. Monel metal has a bright luster, is very resistant to corrosion, and is now widely used in kitchen fixtures

and in corrosion-resistant equipment in chemical industries. Another important nickel alloy is *Nichrome* (§ 499), used in resistance wire for electrically heated stoves, toasters, or flat irons, and for winding small electric furnaces and rheostats.

Nickel is bivalent in most of its compounds. Nevertheless, in an alkaline solution it is readily oxidized to nickelic oxide, Ni_2O_3. When this is dissolved in acids the nickel reverts to the bivalent condition, oxygen being evolved. The reluctance of nickel to assume the tervalent condition or to form complex ions places it in sharp contrast to cobalt.

Nickel salts, when fused with borax, give a *brown bead.* With several organic reagents, nickel salts give colored precipitates, for example, a strawberry-red precipitate with dimethylglyoxime, in a neutral or faintly alkaline solution.

553. The Carbonyls

The carbonyls are a group of interesting compounds, produced by heating certain transition metals to moderate temperatures, in an atmosphere of carbon monoxide. With metals other than iron and nickel the carbon monoxide must be applied under pressure. Each carbon monoxide molecule, $:\overset{-+}{C{\equiv}O}:$, furnishes 2 electrons to form a coordinate bond with a metallic atom.

Enough carbon monoxide molecules are added to give the central atom the electronic structure of the next following inert gas (the outermost groups of electrons containing respectively 18 and 8 electrons). An atom of iron contains 14 and 2 electrons in the two outermost groups, hence needs 5 more pairs of electrons to obtain 18 and 8, and so combines with 5CO to form $Fe(CO)_5$. We may similarly account for:

$$Ni(CO)_4,\ Ru(CO)_5,\ Cr(CO)_6,\ Mo(CO)_6,\ W(CO)_6$$

The three compounds last mentioned are stable crystalline substances, which can be melted and vaporized without being decomposed.

An atom of an element of odd atomic number can acquire the structure just described only by becoming linked with a neighboring atom, through a molecule of carbon monoxide: $\begin{matrix} M \diagdown \\ \quad\ \ C{=}O. \\ M \diagup \end{matrix}$ Thus we account for $Co_2(CO)_9$ and $Mn_2(CO)_{11}$. More interesting yet, analogous compounds exist in which the carbon monoxide is replaced, at least in part, by hydrogen, ammonia, nitric oxide, pyridine, or ethylene diamine, $C_2H_4(NH_2)_2$!

554. Ruthenium, Rhodium, and Palladium (Column 8B)

44	45	46
Ru	Rh	Pd

The six metals of the platinum family form two triads, the light platinum metals (Ru, Rh, Pd) and the heavy platinum metals (Os, Ir, Pt). All six occur together in nature, with platinum predominating, as heavy black grains or in nuggets, in river sands in widely separated parts of the world. Russia and Canada are the principal producers, with Colombia and South Africa following.

The three light platinum metals resemble *silver*, the next element toward the right in the Periodic Table, in readily dissolving oxygen gas, when they are sufficiently finely divided. Like silver, too, they may be dissolved by being heated with oxidizing agents in alkaline media or by fusion with potassium hydrogen sulfate, $KHSO_4$. By such methods they may be separated from the heavy platinum metals which are much more resistant to oxidizing reagents.

Ruthenium combines with oxygen when heated in the air, forming RuO_2, and at higher temperatures yields a volatile, poisonous tetroxide, RuO_4. It is the least useful of all the platinum metals.

Rhodium is ductile, malleable, and sufficiently resistant to oxidation to make it useful for hardening platinum. It may be electrodeposited as a brilliant film, which is so weather-resistant that it is used in jewelry, and for floodlight reflectors, in spite of its high price.

Palladium has the lowest melting point (1550°C) of all the platinum metals. It is slowly attacked by strong acids, and rapidly by aqua regia or chlorine. When it is finely divided (*palladium black*) it strongly absorbs hydrogen—as much as 3000 volumes for each volume of the metal. For this reason it may be used as a substitute for platinum black as a coating for the hydrogen electrode (§ 402).

The *alloys of palladium with gold* (palau, rhotanium) are useful platinum substitutes in dental work, in jewelry, and in crucibles or dishes for the chemical laboratory. In the types of compounds that it forms, Pd^{++} and Pd^{+4}, palladium strongly resembles platinum, just beneath palladium in the Periodic Table.

An easy test for either palladium or platinum begins by evaporating a solution of any of its salts, absorbing the last droplet of liquid in an asbestos fiber and strongly heating the fiber, to decompose the compound and deposit the metal in a finely divided condition. If then held in a mixture of coal gas and air, the fiber glows brilliantly, owing to the catalytic union of oxygen and hydrogen at the surface of the

particles of metal. A very minute trace of either platinum or palladium may thus be detected readily.

555. Osmium, Iridium, and Platinum

76	77	78
Os	Ir	Pt

Osmium is remarkable for its extraordinary density (22.5, which is nearly three times the density of metallic iron and nearly twice the density of lead or mercury). It is the heaviest known substance. Its melting point (about 2500°C) is higher than that of any other member of the platinum group. It readily combines with oxygen, forming a volatile oxide, OsO_4, which is dangerously poisonous, nevertheless used in microscopy (under the name "osmic acid") as a stain for fats. It is an effective catalyst in many different reactions, including the synthesis of ammonia.

Iridium is a hard and brittle metal, with a slight bluish cast. It resists acids, including even aqua regia, but at a white heat is attacked by chlorine and superficially oxidized by oxygen or air. It is useful for alloying with platinum, in quantities usually in the neighborhood of 10 per cent, to produce alloys that are tougher than pure platinum, more resistant to chemical reagents, and less rapidly volatilized at high temperatures. Its price is usually five or six times that of platinum or gold.

Platinum is a silvery white metal, which is readily malleable and extremely ductile. It is resistant to most reagents, and is not oxidized when strongly heated in the air. Nevertheless hot concentrated sulfuric acid slowly attacks commercial platinum (alloyed with iridium). Aqua regia and chlorine dissolve it more readily. It is usually separated from the osmium and iridium that accompany it in nature by being dissolved in aqua regia, the product being a solution of chloroplatinic acid, H_2PtCl_6. On the addition of an ammonium salt a yellow crystalline precipitate of ammonium chloroplatinate, $(NH_4)_2PtCl_6$, is obtained.

Platinum sponge, a porous gray mass, is produced by heating crystals of ammonium chloroplatinate. *Platinum black* is finely divided platinum, obtained by reducing a solution of a platinum salt by formaldehyde or some other vigorous reducing agent. *Platinized asbestos* and *platinized silica gel* are made by moistening asbestos or silica gel (§ 483) with a very dilute solution of a platinum salt or chloroplatinic acid, then heating the material to a sufficiently high temperature to decompose the platinum compound and deposit the metal as platinum

black. Material prepared in this way is an effective catalyst in the production of nitric acid from ammonia (§ 379) and in other important reactions.

Platinum is also used in jewelry and in crucibles and dishes for the chemical laboratory. In using such a crucible or dish one should take care to avoid phosphates, reducible salts of the heavy metals, and any material from which reducing agents may separate elementary phosphates, arsenic, or silicon. Long exposure to a smoky flame will damage platinum ware very seriously.

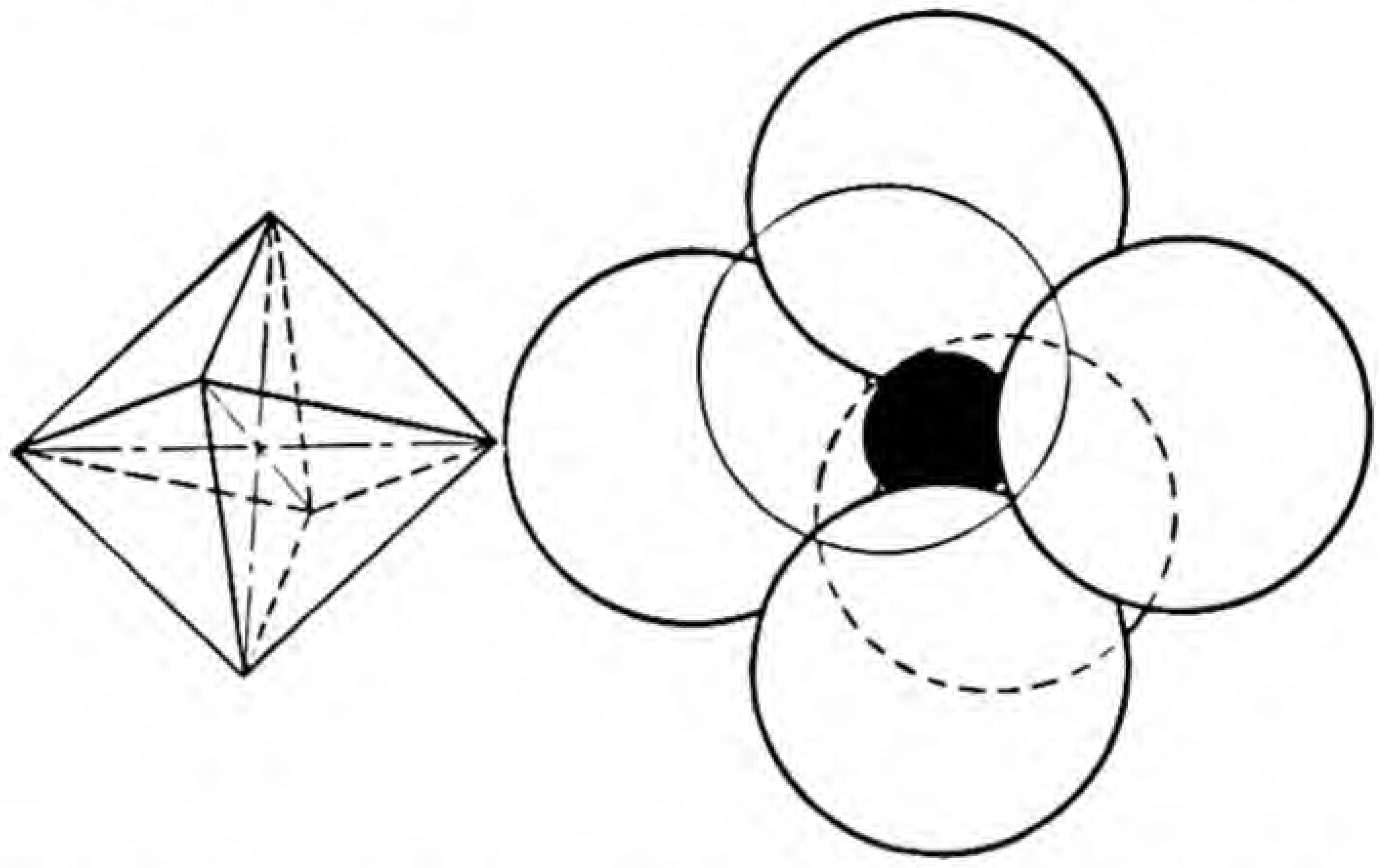


FIG. 174. Octahedral coordination. Six ligands are linked to a central cation at the six vertices of an octahedron.

Platinum forms two series of salts, in which it is respectively bivalent and quadrivalent. In both valence states platinum and palladium both combine with a wide range of neutral molecules and ions to form coordination complexes (§ 250). In the divalent state the central particle (Pt^{++} or Pd^{++}) coordinates four other particles, arranged in a plane at the four corners of a square. In the quadrivalent state the central particle coordinates six other particles, at the six vertices of an octahedron (Fig. 174). Examples:

$$Pt^{++} + 4Cl^- \rightarrow \underset{\text{Chloroplatinous ion}}{PtCl_4^{--}}$$

$$Pt^{++} + 3NH_3 + Cl^- \rightarrow \underset{\text{Triammine-chloroplatinous ion}}{(NH_3)_3PtCl^+}$$

$$Pt^{+4} + 6Cl^- \rightarrow \underset{\text{Chloroplatinate ion}}{PtCl_6^{--}}$$

$$Pt^{+4} + 3NH_3 + 3Cl^- \rightarrow \underset{\text{Triammine-trichloro-platinic ion}}{(NH_3)_3PtCl_3^+}$$

Observe how the charge on the complex ion is altered or reversed as chloride ions, coordinated around the central particle, are replaced by neutral molecules.

The strongest coordinate linkage is 6-coordination, observed with palladium and platinum in the quadrivalent state. Some of these complex ions are so stable that they fail to yield ammonia except to strong acids; and silver nitrate, when added to those that contain chlorine, often fails to produce a precipitate of silver chloride.

556. The Complex Cyanides

The tendency of a central cation to coordinate six other particles, at the six corners of an octahedron, extends to most of the transition elements, but is particularly prominent with chromium and the nine elements of the transition triads. The six outlying particles, often termed *ligands*, become linked to the central particle by coordinate bonds (§ 250). The facility with which such compounds are produced, with chromium and the metals of the transition triads (Group 8B), bears witness that these metals have a particularly flexible electronic structure. Electrons may be transferred from the outer "valence shell" to the underlying incomplete shell of electrons, or conversely, without the expenditure of very much energy. Thus a nearly symmetrical electronic structure may be maintained for the central particle, while it coordinates six outlying particles. If the central particle possessed electrons in very distinct energy levels, rigidly maintained, such an adaptability would not be possible.

A fine example of sixfold coordination is in the ability of metals of the transition triads to combine with the cyanide ion, to form complex ions. The cyanide ion $[:C:::N:]^-$, like the carbon monoxide molecule (§ 553), is a double-ended ligand. In other words, it possesses, at each end, a pair of electrons that may be used to link the ion to a central particle. In the ferrocyanides it is the nitrogen end of the cyanogen that becomes attached to the central ferrous ion:

$$Fe^{++} + 6CN^- \rightarrow \underset{\text{Ferrocyanide ion}}{Fe(CN)_6^{----}}$$

A typical ferrocyanide is potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3H_2O$, a yellow crystalline salt. It is not a double salt, since it does not yield tests for the simple ions that are incorporated in it. It is far less poisonous than the simple cyanides; furthermore, sodium hydroxide and ammonium sulfide, though capable of precipitating ferrous ion, do not affect the ferrocyanide. Even fairly active acids only slowly decom-

pose it, but instead produce a white precipitate of ferrocyanic acid, $H_4Fe(CN)_6$.

Ferric iron similarly coordinates six cyanide groups, to form a complex ferricyanide:

$$Fe^{+3} + 6CN^- \rightarrow Fe(CN)_6^{---}$$

Observe that the only difference between the formulas of the ferrocyanide and the ferricyanide is a difference in charge. Potassium ferricyanide, $K_3Fe(CN)_6$, is a dark red salt, which dissolves to make a solution that appears red or greenish according as light is transmitted through it or reflected from it. *Ferricyanides are intensely poisonous.*

Ferrous salts may be detected by the dark blue precipitate (*Turnbull's blue*) that is obtained on adding a solution of a ferricyanide. Ferric salts may be detected by a similar precipitate (*Prussian blue*), obtained on adding a solution of a ferrocyanide. Observe that *each valence state of iron is detected by adding a reagent that is a complex cyanide, with iron in the other valence state.*

Prussian blue used to be viewed as an ionic compound, ferric ferrocyanide. It is now known to be a three-dimensional network, in which both ends of the cyanogen groups are used in linking ferrous and ferric particles together in a *giant anion*, in which all distinction between ferrous and ferric particles disappears. To produce such a structure the three components Fe^{+2}, Fe^{+3}, and CN^- may evidently enter in various proportions. From what has just been said it is evident that there is no essential difference in structure between Prussian blue and Turnbull's blue. Both show the same diffraction pattern, when examined with X-rays.

557. Other Transition Complexes

Closely related to the complex cyanides, just described, are the complex thiocyanates. In these, the coordinated particle (ligand) is the thiocyanate ion, $\left[\,:\mathrm{C}::\mathrm{N}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{S}}}:\,\right]$, formerly termed sulfocyanate. When a ferric salt is treated with a thiocyanate a deep red color is produced (a delicate test for mere traces of ferric iron). This is due to the formation of the red-colored complex ferrithiocyanate ion:

$$Fe^{+3} + 6CNS \rightarrow Fe(CNS)_6^{---}$$

Similarly, cobalt, in its tervalent state, may coordinate six ions or neutral molecules, such as CN^-, CNS^-, OH^-, NO_2^-, Cl^-, NH_3, H_2O,

and many others, or various combinations of these. Thus complex ions or neutral molecules are formed sometimes so stable as to defy the removal of NH_3 by concentrated acids, the precipitation of Cl^- by silver nitrate, or the precipitation of Co^{+3} by OH^- or S^{--}. The complex cobaltic compounds may be cations, anions, or neutral molecules, according to the proportions in which differently charged ligands are combined with the central particle.

Of interest is the fact that some of these cobalt complexes differ from one another merely in the order of attachment of the six ligands to the central particle. For example, if we have $4NH_3$ and $2Cl^-$, coordinated with a central Co^{+3} particle, the four ammonia molecules may be in one plane, at the four corners of a square (*a*, *b*, *c*, *d*, Fig. 175); or three of them may be at the corners of a square and one of them in another position (for example, *a*, *b*, *c*, *e*); or two of them may be in adjacent corners of a square and the others in two other positions (for example, *a*, *b*, *e*, *f*). The three compounds thus constructed differ in solubility and in other properties. We have here an example of *stereoisomerism* (molecules differing in structure merely in the arrangement of the atoms within the molecule, in space). Sometimes stereoisomerism, among inorganic compounds, results in *optical activity*, as it frequently does among organic compounds.

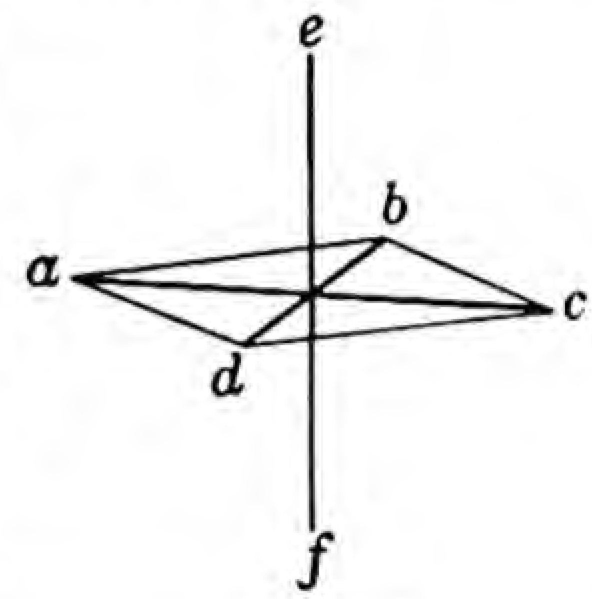


FIG. 175.

Some of the transition complexes bind *water* so firmly that it is removed only with difficulty. An example is seen in hydrated chromic chloride, which is remarkable in existing in three forms, which differ in color, solubility, and chemical properties. In all three forms a central chromic ion is linked with six other particles (H_2O and Cl^-), forming a hydrated or complex ion. Any water not thus linked to the chromium is incorporated in some other manner in the crystal lattice, and any chlorine not thus linked exists as independent chloride ions:

	Cation	*Anions*	*Surplus H_2O*
Violet form......	$Cr(H_2O)_6^{+3}$	$3Cl^-$	
Green form......	$ClCr(H_2O)_5^{++}$	$2Cl^-$	H_2O
Green form......	$Cl_2Cr(H_2O)_4^+$	Cl^-	$2H_2O$

The chloride which is linked with the chromium is firmly bound and no longer ionic, hence is not precipitable by silver nitrate. Accordingly silver nitrate precipitates only two thirds of all the chlorine in the first green form and only one third of that in the second green form.

Observe how the replacement of successive neutral molecules, H_2O, by chloride ions, Cl^- decreases the charge on the cation, from +3 to +2 and finally to +1.

TECHNICAL WORDS

Transition element, p. 641. **Stereoisomerism,** p. 655.

Ligand—any molecule or ion that may become linked with a central particle (by furnishing a pair of electrons to form a coordinate bond). Examples: H_2O, NH_3, CO, CN^-, NO_2^-.

Optical activity—ability to twist the plane of polarization of polarized light through an angle. (See textbooks of organic chemistry.)

Complex ion, p. 492. **Complex salt**—any salt containing complex ions.

For a summary of the preferred system of naming inorganic compounds, including complex ions and salts, consult *J. Am. Chem. Soc.*, **63,** 889 (1941).

EXERCISES

1. Write and balance a valence state equation (§ 266) in which a peroxide oxidizes a ferric salt to a ferrate, and is itself reduced to an oxide.

2. Write an ionic equation, corresponding to the valence state equation just written.

3. Would the reduction of a rare-earth metal from the tervalent to the bivalent condition be accomplished by placing it in contact with cathode or anode? Illustrate by an electronic equation.

4. Write an equation for the reaction of ceric sulfate with a ferrous salt. What fraction of a gram-formula weight of ceric sulfate is needed to prepare a liter of tenth normal oxidizing solution (§ 294)? 100

5. Write an equation for the production of metallic titanium from the dioxide by the thermite process.

6. Write an equation for the hydrolysis of $ZrCl_4$, one product being a hydrous oxide (§ 192).

7. Write an equation for the reaction of vanadium pentoxide with an alkali to form sodium metavanadate.

8. Suggest a method for preparing vanadium trichloride from the pentoxide, similar in principle to the preparation of anhydrous aluminum chloride from aluminum oxide.

9. Write and balance a valence state equation for the conversion of the chromium of chromite ore (ferrous chromite) into a chromate by oxidation by a peroxide.

10. What valence state of chromium is usually obtained when a dichromate serves as an oxidizing agent? Illustrate by an ionic equation for a reaction in which the reducing agent is a sulfite.

11. Write and balance an equation showing the products to be expected when molybdenum disulfide is oxidized by a peroxide, both the elements in the disulfide being raised to their highest valence state.

12. Distinguish between a double salt and a complex salt.

13. Write and balance a valence state equation for the oxidation of manganese dioxide to a manganate by fusion with a nitrate (which is itself reduced to a nitrite).

14. Write an ionic equation to correspond to the valence state equation just written.

15. What fraction of a gram-formula weight of potassium permanganate is needed to prepare one liter of $0.1N$ oxidizing solution? 200

16. By reference to the table of oxidation potentials determine (§ 267) whether ferrous salts should reduce stannic salts or whether the reverse reaction should take place.

17. Write an ionic equation to summarize the conclusion just made.

18. Write an ionic equation to represent oxidation of a cobaltous salt to the cobaltic condition, the oxidizing agent being nitrous acid, which is itself reduced to nitric oxide.

19. Write an ionic equation to represent the precipitation of hydrous nickelic oxide when a nickelous salt is treated with an alkaline hypobromite solution.

20. Show that each atom possesses a complete octet in the formula assigned to carbon monoxide.

21. Show that the metallic atom, in the first three carbonyls listed in § 553, really does possess the electronic structure of the next following inert gas.

22. Write a valence state equation for the oxidation of metallic palladium to the divalent condition, by fusion with potassium acid sulfate, sulfur dioxide being evolved.

23. Write an ionic equation for the reaction just considered. What salt of palladium is formed?

24. Write an equation for the direct union of quadrivalent platinum with ammonia and with chloride ion in such proportions as to form a bivalent complex cation.

25. Write an ionic equation to represent the oxidation of a ferrocyanide to a ferricyanide by chlorine gas, which is itself reduced to a chloride.

26. Tell how you would prepare each substance after the first, in the following list, from the preceding one: chromite ore, sodium chromate (a by-product being hydrous ferric oxide), sodium dichromate, chromium trioxide (CrO_3), potassium chromate, a chromic salt, hydrous chromic oxide, chromic oxide, metallic chromium.

27. What is an alum? Write the formula of an alum containing chromium.

28. What properties of tungsten make it valuable for electric-light filaments?

29. When a solution of a lead salt is treated with a dichromate, lead chromate is precipitated, and an acid is set free. How many equivalents of acid are formed from 100 ml of a $0.01N$ solution of a lead salt? 100

30. What will be the pH of the solution just considered, if its total volume remains 100 ml, assuming that the acid set free is nitric acid? 200

31. Write a valence state equation then an ionic equation to represent the reduction of a chromic salt to bivalent chromium, the reducing agent being metallic zinc in an acid solution.

32. Write an ionic equation for the reaction occurring when ammonium dichromate is heated, assuming the ammonium ion to be oxidized by the dichromate ion, water vapor, and gaseous nitrogen being evolved and chromic oxide left behind. Express as a valence state equation.

33. In a vertical column list all the valence states of manganese considered in this chapter. Indicate by arrows the principal reactions in which one valence state is converted into another.

34. Write ionic or specialized equations for reactions illustrating the following transformations:

$$Mn^{+4} \rightarrow Mn^{+6} \rightarrow Mn^{+7} \rightarrow Mn^{+4} \rightarrow Mn^{+2} \rightarrow Mn^{0}$$

35. A milligram atom of metallic iron is dissolved in an acid, reduced to the ferrous condition, then oxidized by a $0.1N$ oxidizing solution. What volume of the solution will be needed? 100

36. What volume of carbon dioxide, under standard conditions, is evolved by the action of 100 ml of $0.1N$ oxidizing permanganate solution on an excess of an oxalate (§ 294)? 224

37. About where would you place osmium in the electrochemical series? Palladium?

38. Which element has the highest density? The lowest? Which element has the highest melting point? Which element of the platinum group is the most expensive?

39. What percentage of each metal is found in ferrochrome, prepared by reduction of pure chromite ore by the thermite process?

Chapter 40

IRON AND STEEL

558. Occurrence of Iron

Next to aluminum, the most plentiful metallic element is iron. It makes up about 4 per cent of the solid rocks of the earth's crust. Indeed, the magnetic properties of the planet and its high average density support the view that its interior may consist largely of iron. Our sun is a member of a group of dwarf red stars in which iron is revealed by the spectroscope to be very plentiful. Yet, at the temperature of the sun (6000°C, at the surface), iron must exist as vapor.

To be industrially useful, an iron mineral must contain at least 40 to 60 per cent of iron. By far the most important ore is *hematite*, or ferric oxide, Fe_2O_3 (the same chemically as *red ocher*, or *rouge*).

A somewhat hydrated form of this mineral, known as *limonite*, or bog iron ore, is often mined. Magnetic iron oxide, or *magnetite*, Fe_3O_4, is also important. In Europe a large quantity of *siderite*, or ferrous carbonate, $FeCO_3$, is smelted. Iron *pyrite*, FeS_2, consumed in enormous quantities in the manufacture of sulfuric acid, is of no importance as an ore of iron.

559. The Blast Furnace

In ancient times and among primitive tribes at the present day ferric oxide ore has been reduced to spongy iron by being heated with charcoal in a draft of air. Actually the reduction is accomplished by carbon monoxide, in a series of successive reactions. The final result is that expressed by the equation:

$$Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2$$

An excess of carbon monoxide must be used, since the reaction is reversible (§ 338). Primitive iron furnaces were never hot enough to melt the iron thus produced, but by heating the lumps of spongy iron and pounding them on an anvil they were readily compacted into *wrought iron*, some of which was of excellent quality, though usually rendered unreliable by impurities, including considerable amounts of slag.

From primitive iron furnaces at length evolved the modern blast furnace, shown in cross section in Fig. 176. Raw materials are *ferric oxide ore*, *limestone*, and *coke*. Separate carloads of these are hauled to the top of the furnace by the inclined track and cable shown in our sketch, and dumped into the furnace through a hopper designed to admit this material yet prevent the escape of furnace gases.

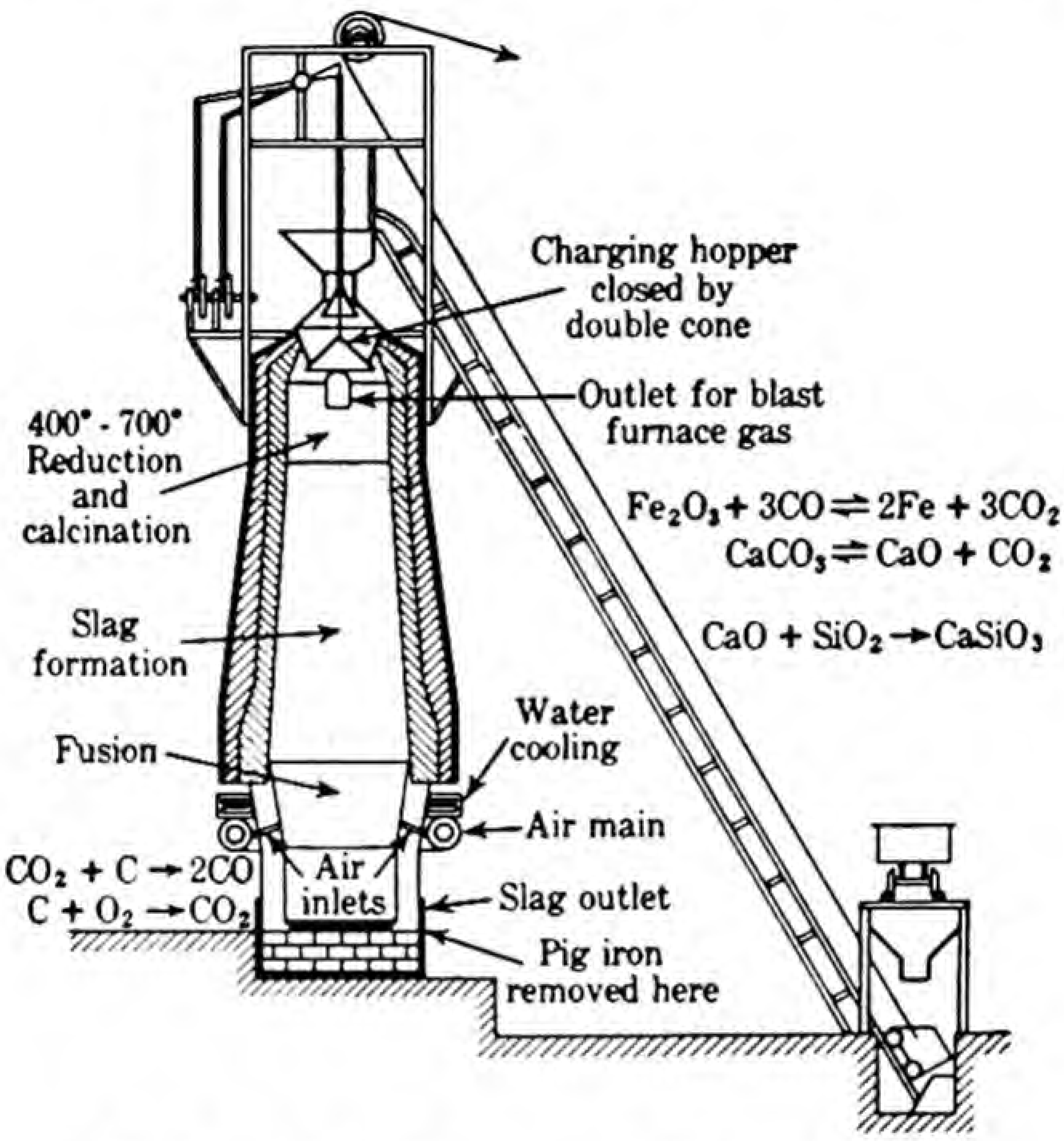


FIG. 176. Cross section of a blast furnace.

Observe what happens in four separate regions or zones:

1. In the upper region of the furnace, where the temperature is 400° to 700°, the ferric oxide ore is reduced by carbon monoxide to magnetic iron oxide, ferrous oxide, and eventually to spongy metallic iron. In this zone the limestone, added to serve as a flux (p. 516), parts with carbon dioxide, and is converted into quicklime, CaO (Ex. 1, 2.)

2. In the middle region of the furnace, the quicklime unites with the siliceous impurities of the ore, to form a slag, consisting largely of calcium metasilicate, $CaSiO_3$.[1]

3. Just below the middle of the furnace, at its widest part, the temperature reaches and exceeds the melting point of impure iron. The

[1] If the impurity present in the ore happens to be limestone, the flux used will be sand or feldspar. If the ore is quite pure, both sand and limestone must be added, to form enough slag to cover over the molten iron in the bottom of the furnace and prevent it from being oxidized.

reduced iron and slag both melt in this zone. The contraction of the furnace walls below this point is to allow for the decrease in volume due to fusion.

4. Near the bottom of the furnace *dry, preheated air* is blown in. Here vigorous combustion takes place. Since air is present in excess, the first product of the combustion is carbon dioxide. But as this passes upward through the overlying layer of white-hot coke, it unites with the latter to form carbon monoxide, which serves for the reduction of the iron ore in the top part of the furnace. (Ex. 3, 4.)

A large blast furnace may require 1000 tons of iron ore in a day, 500 tons of coke, 250 tons of limestone, and 2500 tons of air. It will produce 550 tons of pig iron every 24 hours, running continuously day and night for several years, until it finally needs to be shut down for renewal of the furnace lining. The air blast is freed from moisture by being cooled by circulating cold brine, previous to being heated in the stoves. Several tons of moisture are condensed and removed, in drying the blast, every 24 hours. The operation of the furnace is thus made very much more efficient, for in the presence of moisture the working temperature of the furnace is reduced, because heat disappears in the reaction of moisture with coke, forming water gas (§ 87).

Near the bottom of the furnace, *slag* trickles out in a steady stream. At a somewhat lower level, molten *pig iron* is withdrawn, at intervals. The slag is an almost useless by-product, though it is sometimes converted into mineral wool, paving stone, or cement. The torrent of *blast-furnace gas* issuing from the top of the furnace is of very low fuel value, since it consists largely of nitrogen and carbon dioxide (N_2, over 50 per cent; CO_2, 25 per cent; CO, about 20 to 25 per cent). Nevertheless it is burned as fuel in huge stoves, used for heating the air blast of the furnace, leaving a surplus for raising steam and other uses. (Ex. 5, 6.)

560. Pig Iron, Cast Iron, and Wrought Iron

The blast furnace produces *pig iron*, which is very impure iron, usually containing 3.5 to 4 per cent carbon and 0.75 to 2.00 per cent silicon, with smaller amounts of sulfur, phosphorus, and manganese. These impurities lower the melting point of iron from about 1530° to about 1130°C, and seriously decrease its strength. The lowered melting point is desirable, since it is extremely difficult to maintain a temperature as high as 1530°C by burning fuel, even though the air blast is dried and preheated; for combustion of carbon monoxide at such high temperatures is incomplete, because reversible (Van't Hoff's

Principle, § 346). It is very necessary that both the slag and the impure iron be kept completely molten, so that they may form separate layers in the bottom of the furnace.

Pig iron has no very considerable tensile strength. Nevertheless its low melting point makes it valuable, when mixed with scrap iron or scrap steel, for casting steam radiators, window weights, and similar objects not subject to great tension or sudden shocks. The result is *cast iron.* According to its content of carbon, silicon, and manganese, and its rate of cooling, it may contain carbon chiefly as flakes of graphite (*gray cast iron*) or chiefly as cementite, Fe_3C, or in solid solution (*white cast iron*).

Malleable iron is made from cast iron with a low content of phosphorus, remelted in a small furnace, and adjusted in composition until it contains about 1.00 to 1.25 per cent silicon and 2.75 to 3.00 per cent carbon. When castings made from this material solidify quickly the carbon remains combined with the iron, as Fe_3C; but when the castings are reheated (670° to 870°C) for several days in closed pots the carbon separates as microscopic grains of graphite. The resultant product is stronger than gray cast iron, less brittle than white cast iron, and cheaper than steel. Agricultural implements, tools, and machine parts not subject to sudden shocks or severe strains are frequently made of this material. It may be shaped by punching or stamping, but cannot be welded or forged, since the high temperature needed in these processes causes the carbon to revert to the combined form, as in white cast iron.

Wrought iron is made from pig iron by oxidizing and so removing a considerable part of the carbon, silicon, and manganese contained in the pig iron as impurities. The oxidizing agent, as the process was first developed, over a century and a half ago, was ferric oxide, added as rusty scrap iron or hematite ore. In the Aston process, now widely used, the impurities are burned away in a blast of air, in the presence of a little limestone, used as a flux, as in making Bessemer steel. The purified iron produced by either process needs to be worked with a steam hammer, while still white hot, to squeeze out most of the slag (ferrous, manganese, and calcium silicates) that is produced by oxidizing the silicon of the pig iron (Ex. 7, 8.)

561. Four Methods for Making Steel

To convert iron into steel, two steps are necessary:

1. Oxidize and remove most of the impurities in the iron, especially silicon, sulfur, and phosphorus.

2. Add a definite proportion of carbon, and usually a little manganese (intended chiefly to deoxidize the steel).

The properties of the finished steel will depend on the thermal and mechanical treatment that it receives—whether it is cooled slowly from a high temperature or is quenched (§ 563); and whether it is rolled, hammered, or drawn at any stage of its cooling.

Different steel-making processes differ in the method by which the impurities in the pig iron are oxidized, in the type of flux added to slag off the oxidized impurities, and in the care that is possible in controlling the composition of the final product. There are four chief processes:

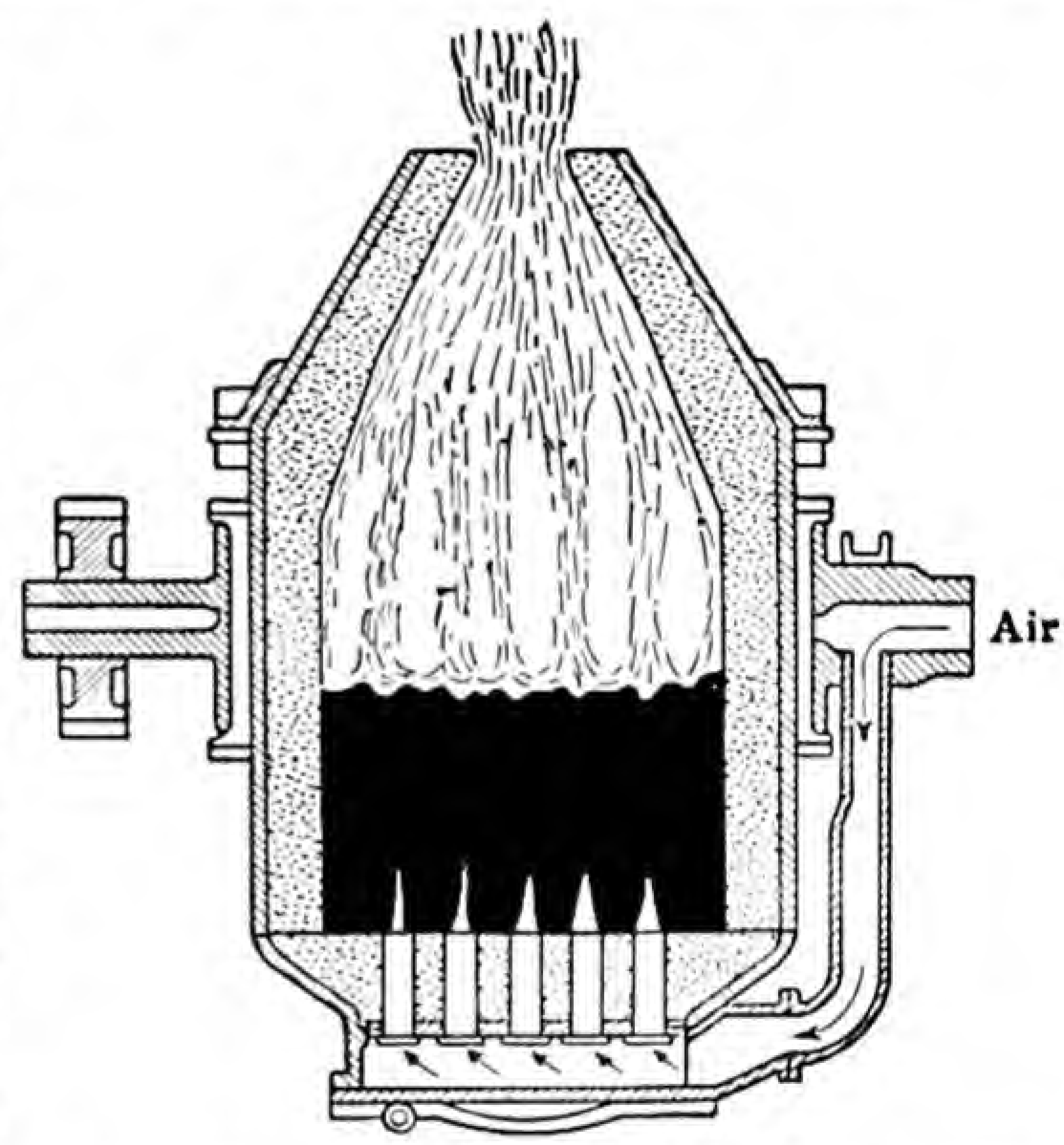


FIG. 177. Cross section of Bessemer converter.

1. *Crucible steel* (now nearly obsolete) was made by melting wrought iron or mild steel in a closed, fireclay-graphite crucible, in contact with charcoal. Carbon penetrated the metal, forming steel that contained 0.75 to 1.5 per cent carbon, present as a solid solution. Crucible steel is highly uniform in quality, and free from slag and dissolved gases. It has been used for watch springs, razors, knives, and similar objects in which uniform quality, surface hardness, or ability to be sharpened to a keen edge happened to be of importance. It is too brittle and too expensive to be used for rails or engineering structures.

2. *Bessemer steel* is produced by a process that begins by blowing a blast of air through 10 to 25 tons of molten pig iron, contained in a Bessemer converter (Fig. 177), in the presence of a flux of silica, lime, or magnesia, as the case may require. Carbon, silicon, and phosphorus, contained in the pig iron as impurities, are oxidized by the oxygen of the air blast. Carbon monoxide escapes and burns as a torch of flame at the mouth of the converter, and the silica and phosphorus are removed in the slag:

$$2C + O_2 \rightarrow 2CO \uparrow$$

$$Si + O_2 \rightarrow SiO_2 \qquad SiO_2 + CaO \rightarrow \underset{\text{(Slag)}}{CaSiO_3}$$

$$4P + 5O_2 \rightarrow 2P_2O_5 \qquad P_2O_5 + 3MgO \rightarrow \underset{\text{(In slag)}}{Mg_3(PO_4)_2}$$

The oxidation of the carbon and silicon releases sufficient heat to maintain the iron in a molten condition until the oxidation is completed (about 7 to 15 minutes).

After carbon and silicon have been burned out, as just described, an appropriate quantity of *spiegeleisen* (an alloy of iron with 5 to 15 per cent manganese and several per cent carbon) is added. This gives the finished steel the desired percentage of carbon. The manganese in the spiegeleisen reduces any ferrous oxide that may have been produced by the blast of air. Dissolved or combined oxygen or nitrogen that may still remain is then often removed by adding metallic aluminum to the finished steel; then the slag of aluminum oxide and nitride that rises to the top is skimmed off. (Ex. 9.)

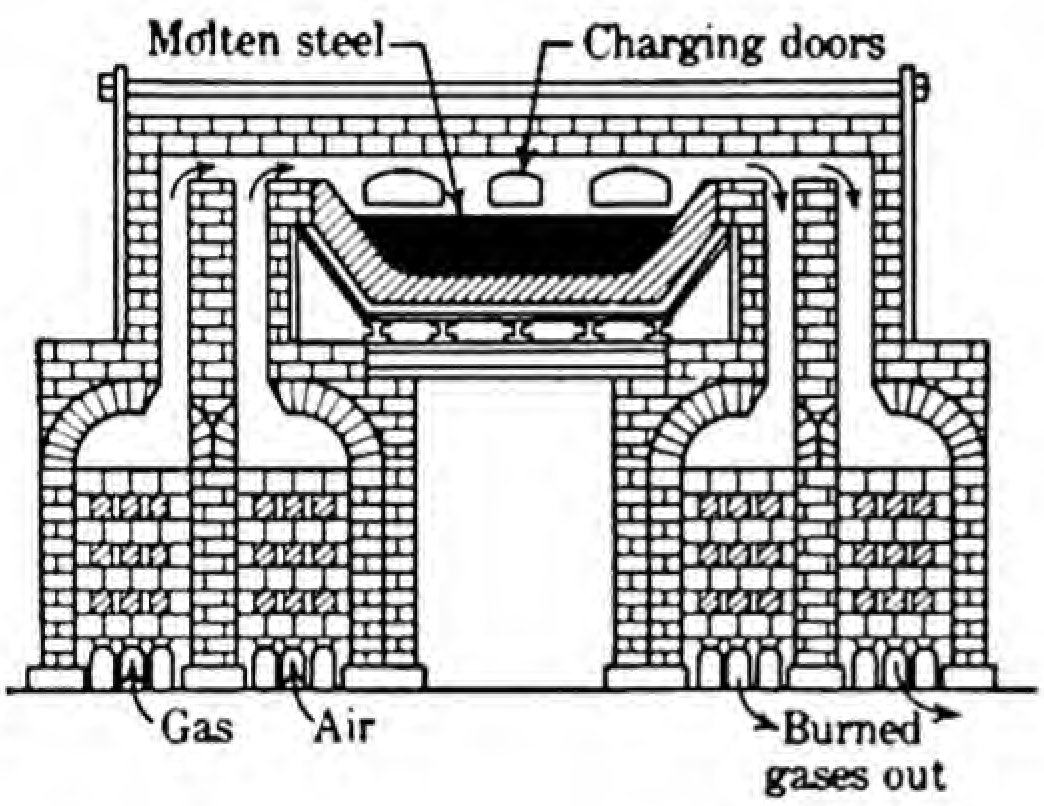


FIG. 178. Cross section of open-hearth furnace. Observe that the incoming gas and air are preheated, by being passed over hot brickwork in a *regenerator*. The burned gases pass out through a similar chamber, heating the brickwork in this. When the brickwork in the first chamber has been somewhat cooled, that in the second chamber has become white hot. The direction of flow of gases through the chambers is then reversed.

3. *Open-hearth steel* is made in a furnace of 50 to 100 tons capacity (Fig. 178), in which the oxidizing agent (to oxidize carbon and silicon) is ferric oxide (in the form of rusty steel scrap and hematite ore):

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \uparrow$$

$$\left.\begin{array}{r} 2Fe_2O_3 + 3Si \rightarrow 4Fe + 3SiO_2 \\ CaO + SiO_2 \rightarrow CaSiO_3 \text{ (slag)} \end{array}\right\}$$

If the furnace has a basic lining and a basic flux (CaO and MgO) any phosphorus that may be contained as an impurity in the pig iron is oxidized and removed as calcium or magnesium phosphate. (Ex. 10.)

The open-hearth process produces more uniform steel than the Bessemer process, and can operate on raw materials that contain a higher percentage of impurities. It is also less likely to have defects caused by bubbles of air or particles of slag, trapped in the molten metal.

4. *Electric steel* is produced by further purification of Bessemer or open-hearth steel, in an electric furnace in which a reducing atmosphere

is maintained by carbon, in the presence of lime or magnesium. This method has the advantage of removing sulfur, which is slagged off as calcium or magnesium sulfide. Electric steel has now very largely displaced crucible steel in the production of tools and other high-priced articles.

562. Effect of Impurities and Alloying Elements in Iron and Steel

Mere traces of impurities in iron or steel may greatly alter its properties. Particles of slag or graphite may seriously increase the tendency to corrosion (§ 504). A few hundredths of one per cent of copper, on the contrary, greatly decreases the tendency of sheet steel to corrosion. Larger quantities of certain alloying elements (nickel or chromium, for example) improve resistance to corrosion, by giving a more homogeneous product, or by inducing crystallization in a more stable form, or by so altering the electron-atom ratio (§ 497) that the electrical conductivity of the material is reduced. (Ex. 11.)

Certain impurities tend to separate as weak intercrystalline material, hence reduce the strength of iron or steel. Phosphorus, even in traces, greatly weakens steel at ordinary temperatures. Sulfur has the same effect on steel that is red hot.

Air, present as small blowholes in improperly deoxidized steel, is a serious menace to its strength. So is ferrous or manganous oxide. Bessemer steel, when first poured from the converter, is therefore commonly treated with a *scavenger element* (such as Al, Ti, Mn, V) to combine with and so remove oxygen and nitrogen. The process, moreover, releases so much heat that the fluidity of the steel is increased, and slag separates more completely. Silicon, sometimes added to steel as a deoxidizer, also furthers the precipitation of carbon as graphite from steel that would otherwise be hardened by retaining carbon as a solid solution.

Sometimes strength and a certain degree of flexibility need to be possessed by steel, together with surface hardness (in axles, for example). To attain this result a strong and flexible "mild steel" (low-carbon steel) is used, which is given a very thin coating of harder material by case hardening or nitriding. In *case hardening* the steel is heated for some hours in a closed box containing charcoal and barium carbonate. These materials react to form carbon monoxide, which penetrates the steel to about the thickness of a sheet of paper, and reacts with the iron to form cementite, Fe_3C, which is very hard. In *nitriding*, steel of special composition is heated to about 630°C in an atmosphere of ammonia, for a period of 2 to 90 hours, according to the depth to

which the treatment is to penetrate. The hardening is due to the formation of a very hard iron nitride (an interstitial compound, § 499). (Ex. 12.)

Metals that are added to steel not merely to deoxidize it but to form alloys (Cr, Ni, W, Mo, etc.) alter the temperature at which the different allotropic forms of iron are converted into one another (§ 563), and frequently cause crystalline phases to appear that are unknown in simple steels. Alloy steels therefore possess a wide range of special properties, briefly reviewed in § 564.

563. The Iron-Carbon Diagram

Iron, like carbon, sulfur, phosphorus, and many other elements, exists in different allotropic forms, having distinct physical properties. The ordinary form of iron and the principal component of wrought iron is soft, ductile, easily magnetized, and strongly attracted by a magnet. It is called α-ferrite. When this is heated it passes through two different transformations, and above 920°C becomes γ-ferrite, which is denser and non-magnetic. This transformation is shown at T, at the left-hand margin of the accompanying *phase diagram* (Fig. 179).

Now γ-ferrite can dissolve a varying amount of carbon, according to the temperature, to form a solid solution called *austenite*, the limits of whose composition at different temperatures are shown by the boundaries of an area at the left-hand margin of our diagram. We see that the maximum amount of carbon that may be thus dissolved in iron is about 1.9 per cent, at 1130°C. Any extra amount of carbon beyond this percentage must separate as a distinct phase, normally as cementite, Fe_3C, which contains about 6.7 per cent carbon, and is represented by the right-hand margin of our chart.

The area marked *Liquid* represents the range of temperature and composition within which mixtures of iron and carbon are completely liquid. If we cool molten iron containing 1.9 to 4.2 per cent carbon, as represented by the vertical line UV, freezing will begin at the temperature represented by V, with the separation of austenite of the composition W. Continued lowering of the temperature causes the composition of the liquid to vary along the line VE, until the *eutectic temperature* (p. 669) is reached at E. The composition of the austenite that meanwhile separates will vary along the line WF.

If we cool a liquid containing over 4.2 per cent carbon, as represented by the vertical line XY, freezing will begin at Y, usually with the separation of cementite. Continued cooling, below the temperature represented by Y, then causes the composition of the liquid to vary

along the line *YE*, while cementite separates, with a nearly constant composition, as represented by the vertical line at the right-hand margin of the chart.

This still leaves us to tell what happens after the liquid iron has arrived at the eutectic temperature and eutectic composition, *E*, by

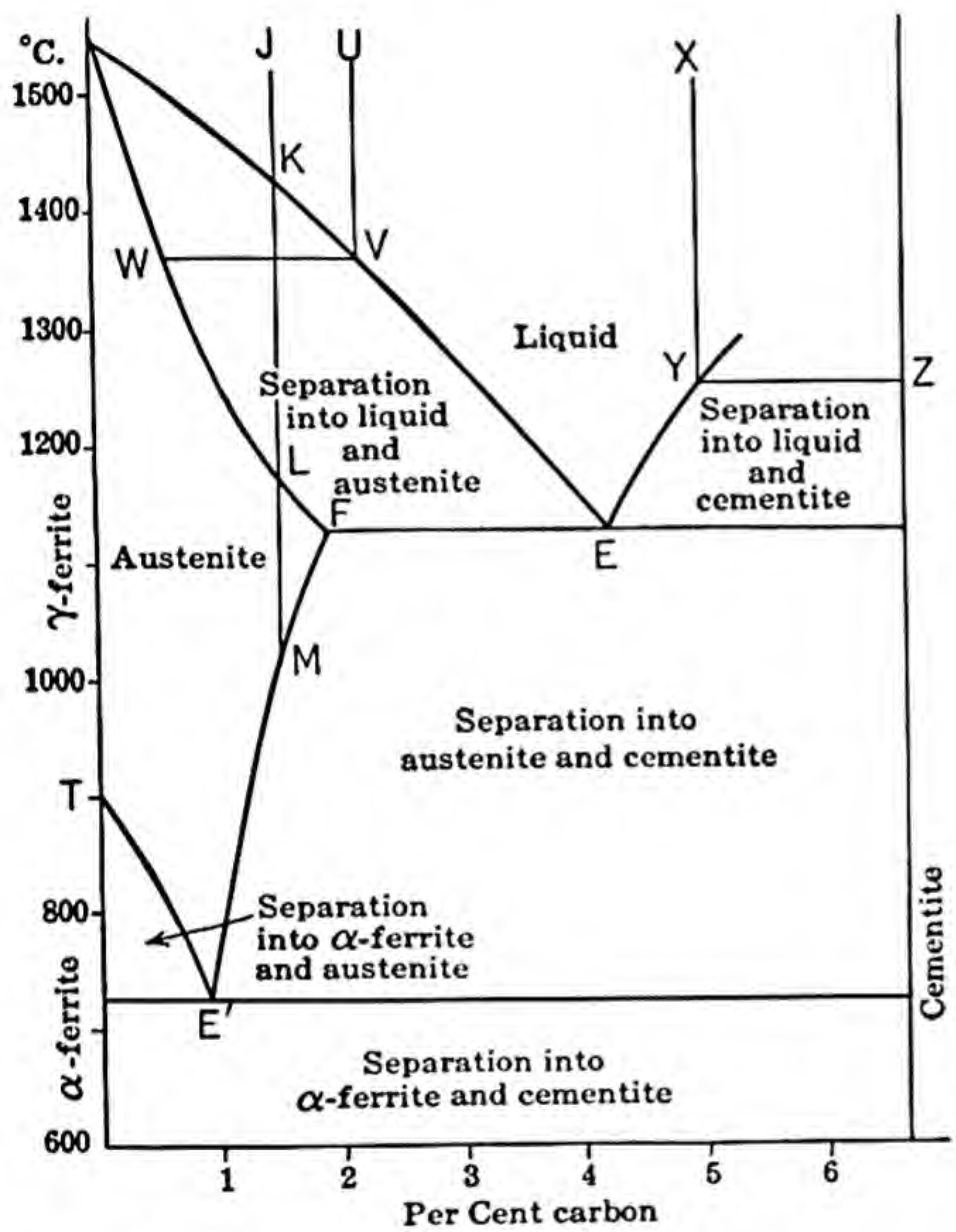
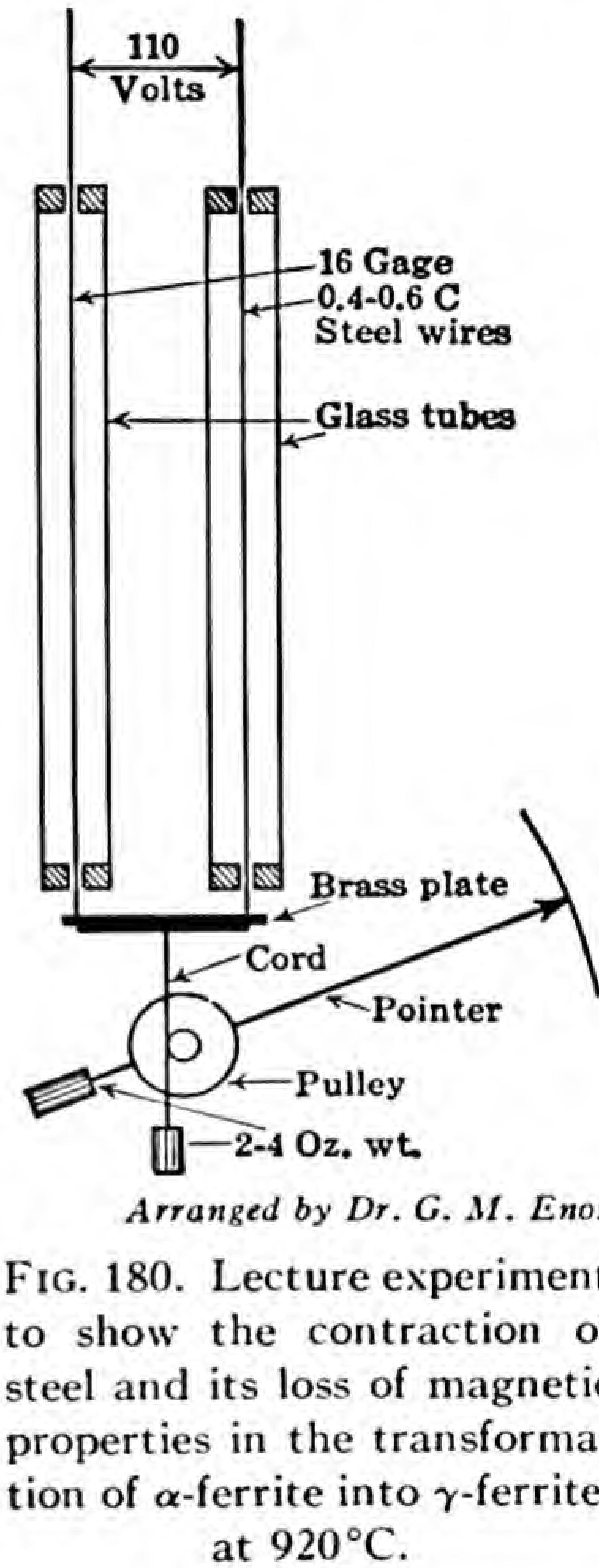


FIG. 179. Iron-carbon phase diagram.



Arranged by Dr. G. M. Enos

FIG. 180. Lecture experiment to show the contraction of steel and its loss of magnetic properties in the transformation of α-ferrite into γ-ferrite, at 920°C.

either of the two routes just indicated. Ordinarily the temperature then remains constant at the eutectic temperature, 1130°C, as heat is gradually lost and solidification continues, both austenite and cementite separating at the same time, in nearly equal proportions. If the solidified but still white-hot steel is then very suddenly cooled (*quenched*), the character that the material had at high temperatures will be retained at room temperature, and examination of a polished specimen of the steel, under a microscope, will show a mosaic pattern, with areas of *martensite* (quenched austenite), scattered among areas of *cementite*.

In conclusion, let us follow the course of cooling of a steel containing only 1.5 per cent carbon, represented by the vertical line JK. Freezing begins at the temperature represented by K and is completed at L. The steel is then solid austenite. If it is suddenly quenched it will retain the structure of austenite, down to room temperature. But, if it is slowly cooled, a temperature M is finally reached at which the austenite must part with some of its carbon, which separates as cementite. The composition of the austenite then gradually varies along the line ME', until we reach the *eutectoid temperature* (p. 670), 725°C, represented by the point E'. The temperature then remains constant again, as heat is slowly withdrawn, while the austenite that still remains is decomposed, forming material which because of its pearly luster has been termed *pearlite*. Examination under a high-powered microscope (magnification, about 600 diameters) reveals that pearlite does indeed resemble mother-of-pearl in consisting of a series of nearly parallel wavy lines, of alternate dark and white material. In mother-of-pearl these bands are of dark organic material, alternating with white bands of calcium carbonate. In steel they consist of ridges of hard cementite, alternating with grooves of soft α-ferrite (Fig. 181).

FIG. 181. A polished and etched steel specimen, magnified 600 diameters. At the top we see an area of austenite. Below this is the zebra-like pattern of pearlite.

The main point of all this is that steel which has been suddenly cooled from a high temperature will contain most of its carbon in the form of a solid solution (austenite or martensite) and will have the *hardness* and *brittleness* characteristic of that material. Steel that has been slowly cooled, however, will have had time to permit at least partial transformation of austenite into pearlite. If it contains less than 0.9 per cent carbon (a *hypo-eutectoid steel*) it will contain areas of α-ferrite, among areas of pearlite; if it contains more than 0.9 per cent carbon (*hyper-eutectoid steel*) it will contain areas of cementite, scattered among areas of pearlite. In either event it will possess the *softness* and *ductility* that is characteristic of α-ferrite, together with a certain amount of hardness, due to cementite.

By an intermediate rate of cooling, steel of an intermediate quality may be prepared. Under the microscope it then reveals a structure intermediate between martensite and pearlite, the sequence of changes

being martensite → troostite → sorbite → pearlite. These names refer to different microscopical appearances, representing successive stages in the transformation of a uniform solid solution into pearlite.

It is also possible to alter the properties of iron by having some of the carbon separate in the form of graphite, as it is inclined to do in the presence of silicon. Some details have already been given in our discussion of cast iron (§ 560).

564. Alloy Steels

Alloy steels are made by the addition of other elements than carbon and the small percentage of manganese always present in simple steels. The properties of alloy steels depend quite as much on the heat treatment (quenching, tempering, and annealing) that the metal receives as on its chemical composition. It is incorrect to state that one element produces a given effect on the mechanical properties of steel and that another element has a different effect. In most instances a desired result can be obtained with several different steels of widely different composition, by using the heat treatment proper to each.

Element Added to Steel	*Percentage*	*Properties*
Manganese	11–14	Hard surface, resistant to wear.
Chromium	$1\frac{1}{2}$–2	Hard surface, tough and strong.
	10–15	With less than 0.1 per cent carbon. "Stainless steel."
Nickel	2–4	High tensile strength. Resistant to corrosion. Small coefficient of expansion.
Silicon	1–2	Hard. Not easily broken by flexure. Low energy loss when used in electrical transformers.
Tungsten	4–6	Hard. Retains its temper when heated.

Recently, *nickel-clad steel plate* has been widely used. The bond between the two metals is perfect and does not fail when the material is rolled or twisted. Thus the strength of steel is combined with the rust-resistant and acid-resistant properties of nickel. (Ex. 13–18.)

Technical Words

Case hardening, p. 665. **Nitriding,** p. 665.

Phase diagram—a diagram to show the range of composition and temperature (or pressure) within which any given set of phases are in equilibrium.

Eutectic—a mixture of two solids, concurrently deposited from a liquid solution, as heat is withdrawn, the temperature remaining constant.

Eutectic temperature—the temperature at which a liquid solution is in equilibrium with a mixture of two solids, having certain components in common with the liquid.

When a liquid is cooled there is a retardation in the rate of cooling when freezing begins, some particular solid being deposited; when the temperature has further fallen to the eutectic temperature a new solid begins to separate, and the temperature thereafter remains constant, while both solids separate together, until solidification is complete.

Eutectoid—a mixture of two solids, concurrently separated from a solid solution, as heat is withdrawn, the temperature remaining constant. Pearlite is a eutectoid mixture of α-ferrite and cementite, separated from the solid solution called austenite (§ 563).

Eutectoid temperature—the temperature at which a solid solution is in equilibrium with a mixture of two solids, having certain components in common with the solid solution.

Scavenger element—an element added to steel to combine with and so remove oxygen and nitrogen and sometimes also to facilitate the separation of slag.

Ferrite, pure iron. If magnetizable but incapable of dissolving carbon it is called α-ferrite. If not magnetizable, but able to dissolve carbon up to about 1.9 per cent, it is called γ-ferrite.

Austenite—a solid solution of carbon in γ-ferrite.

Martensite—quenched austenite. Successive stages in its transformation to pearlite are known as **troostite** and **sorbitel.**

Pearlite, p. 668. **Cementite,** p. 662.

Hypo-eutectoid steel—steel containing less than 0.9 per cent carbon (that being the percentage of carbon in the eutectoid mixture, pearlite).

Hyper-eutectoid steel—steel containing more than 0.9 per cent carbon.

Exercises

1. Write equations for the reduction of ferric oxide to metallic iron, in the blast furnace, in the three separate stages indicated in the text.

2. What weight of hydrated ferric oxide, $Fe_2O_3 \cdot H_2O$ containing 25 per cent silica as an impurity, is needed to produce a ton of iron? 212

3. Write equations for the production of carbon dioxide and the reduction of this to carbon monoxide, in the blast furnace.

4. Write an equation for the formation of slag from limestone, present in an iron ore as an impurity.

5. Write an equation for the production of water gas.

6. When blast-furnace gas, containing 20 volume per cent carbon monoxide, is burned, what volume of air is needed for every 1000 cubic feet of gas? 476

7. Write an equation showing the production of carbon monoxide from the carbon of pig iron, in the manufacture of wrought iron, as first developed. Explain why more than one ton of wrought iron was obtained from each ton of pig iron used.

8. Write equations for the oxidation of silicon and its removal as slag, in the Aston wrought-iron process.

9. Write equations for the reactions that take place on adding aluminum to Bessemer steel.

10. Write equations for the oxidation of phosphorus, forming P_2O_5, and its removal in the slag, in the open-hearth process.

11. Explain why particles of slag or graphite tend to increase the rate of corrosion of steel.

12. Which elements form interstitial compounds with others? What physical properties do such compounds generally possess?

13. Which of the following are conspicuously hard and brittle, and which soft and ductile: α-ferrite, austenite, cementite?

14. Explain why quenching of white-hot steel results in a hard and brittle product, whereas slow cooling gives a soft and malleable product.

15. Explain why wrought iron (§ 560) cannot be hardened by quenching.

16. What is the scale that accumulates on the surface of steel, when white-hot billets are rolled into sheets? How is this scale commonly removed?

17. Explain why it is not possible to operate a blast furnace so that only nitrogen and carbon dioxide are contained in the blast-furnace gas.

18. What would be the result, and how might the blast furnace need to be modified, if oxygen were used instead of air?

Chapter 41

THE POST-TRANSITION METALS

565. General Characteristics

With group 8, in the middle part of the Periodic Table, an incomplete group of electrons, next below the outermost group, becomes complete. From this point onward, as we pass through the table, from left to right, the outermost group of electrons is built up steadily, from one electron (group 1B) to eight electrons (group 0). This rapid increase in the number of valence electrons causes a rapid passage from the metallic condition (groups 1B and 2B) to the non-metallic condition (groups 7A and 0). In the intervening groups metallic character is limited to the elements of highest atomic number.

The decrease in metallic character with increasing number of valence electrons is not difficult to explain. It is simply that a higher relative number of electrons permits a greater proportion of them to be used in establishing covalent bonds between each atom and its neighbors. Electrical and thermal conductivity consequently fall off, and the crystal structure passes over from the close-packed yet deformable structure characteristic of metals through the rigid covalent structure of the diamond, to crystals in which the structural units are molecules (S_8 and I_2, for example).

The possession of *complete* inner shells of electrons by the post-transition metals has several other effects worth keeping in mind. For one thing, it results in *decreased tendency toward variable valence.* Compare the post-transition elements zinc and cadmium (which have an invariable ionic valence of +2) with the transition elements manganese and chromium (which in addition to an ionic valence of +2 may possess covalence corresponding to a wide range of valence numbers). The completion of the inner group of electrons evidently stabilizes the outermost group and tends to limit valence to some one value.

Furthermore, a complete inner group of electrons tends to shield outlying electrons and neighboring atoms from the attraction of the heavily charged nucleus. In consequence, the post-transition metals

do not form complex ions of anything like the stability observed with cobalt and platinum, for example (§§ 552, 555). Finally, we shall see (§ 568) that complete groups of electrons result in *colorless ions*. The only colored ions formed by the post-transition metals are those of gold and bivalent copper!

566. Metallic Copper and Its Alloys

Copper is occasionally found in nature uncombined with other elements. The most important copper ores, however, are complex oxides and sulfides (occasionally silicates and carbonates), in which copper is associated with iron, nickel, or lead, with smaller quantities of silver and gold. The amount of copper in these ores is frequently not above 5 per cent.

Recovery of copper from low-grade ores begins with concentration by froth flotation, followed by roasting (§ 507). The roasted concentrates are melted in a small furnace, in the presence of a siliceous flux. The more readily oxidizable metals, including most of the iron, enter the slag as silicates. Beneath the slag is a layer of heavier material called *matte*, which consists of a readily fusible mixture of cuprous and ferrous sulfides, containing sulfides of gold, silver, and nickel, together with a part of the zinc, lead, antimony, and arsenic contained in the original ore. (Ex. 1.)

The matte is ordinarily transferred to a converter much like that used in the production of Bessemer steel (§ 561), and oxidized by a blast of air, in the presence of a siliceous flux. This removes most of the sulfur, arsenic, and oxidizable metals, which enter the slag as fusible silicates. The *blister copper* thus obtained is further purified by gentle oxidation, then treated with green wood or reducing gases to reduce any cuprous oxide that may have been formed in the process of oxidizing and slagging off the more readily oxidizable metals. The product thus obtained is cast into anodes and purified by electrolysis, as already described (§ 522). (Ex. 2, 3.)

Metallic copper and many of its alloys are remarkably tough and strong. Some alloys have a tensile strength greater than that of structural steel. In general, *copper and its alloys are applied to uses that put a premium on the qualities in which copper is superior to iron and steel: ductility, malleability, resistance to corrosion, and high electrical conductivity.* Its ready deposition by electrolysis leads to its use for *electrotypes*—electrodeposited copper plates from which this book and textbooks in general are printed. Copper electrotypes wear longer than zinc etchings, and call for a smaller investment of capital than

would be needed were the original type metal held over for a period of a year or more, between successive printings.

Bronze is a copper alloy containing tin and sometimes zinc. It is much harder than pure copper, and is a substitute for steel in castings requiring mechanical strength, but in which even a small amount of rusting would be objectionable (laundry machinery, propeller blades, paper pulp beaters). Large quantities are used in coins and statuary.

Brass contains copper and zinc (details in § 498). It is greatly inferior to pure copper in strength and pliability, but melts at a lower temperature, is easily cast and machined, and does not rust. But in contact with metals below it in the Electrochemical Series it is readily attacked, the zinc disappearing in a very short time, leaving a spongy mass of copper. Alloys of copper with other metals have already been listed (§ 499). (Ex. 4.)

567. The Chemical Characteristics of Copper

Copper, silver, and gold have some of the characteristics of the transition metals which immediately precede them in the Periodic Table. In other words, copper has some resemblances to nickel, silver to palladium, and gold to platinum in the types of compounds that they form. All three metals resemble the transition metals in variable valence, in capacity for forming stable complex ions, and (except for silver) in the ability to form colored ions.

	1B
At. No.	29
	Cu
	47
	Ag
	79
	Au

With copper we have cuprous salts, Cu^+, in which the metallic atom, by loss of a single electron, has acquired a stable outer group of 18 electrons. In cupric salts, Cu^{++}, a second electron has been lost, resulting in a regrouping of the remaining electrons and the development of a blue color. So little energy is required to remove this second electron that cuprous salts, unless carefully dried and protected from moisture, are quickly oxidized to the cupric condition by the oxygen of the air.

Cupric salts, on the contrary, are, by sufficiently vigorous reductants, reduced to the cuprous condition. An excess of an iodide, for example, on being added to a dilute cupric solution, reduces the copper to the lower valence, then precipitates it as cuprous iodide, CuI (white):

$$Cu^{++} + I^- \rightarrow Cu^+ + \tfrac{1}{2}I_2$$

$$Cu^+ + \underset{\text{(Excess)}}{I^-} \rightarrow CuI \downarrow$$

The iodine set free in this reaction may be titrated with a standard thiosulfate solution (§ 314). From the volume of this needed it is easy to deduce the amount of copper in the original solution. (Ex. 5.)

The double valence of copper leads to its rapid corrosion in the presence of acids and cupric salts. First the cupric salt reacts with the metallic copper and is reduced to a cuprous salt:

$$Cu^{++} + Cu^0 \rightarrow 2Cu^+$$

Then the cuprous salt is reoxidized by the oxygen of the air:

$$2Cu^+ + \underset{\text{Air}}{\tfrac{1}{2}O_2} + \underset{\text{Acid}}{2H^+} \rightarrow 2Cu^{++} + H_2O$$

Then the cupric salt reacts with more copper. So the action goes round and round until all the metal is dissolved. Scrap copper is converted into copper sulfate, commercially, by being dissolved in dilute sulfuric acid in the presence of copper sulfate and a current of air, in spite of the fact that copper occupies a position below hydrogen in the electrochemical series.

Copper forms deep blue solutions, containing the tetrammine cupric ion, $Cu(NH_3)_4^{++}$ (§ 364), when an excess of ammonium hydroxide is added to a cupric solution. By adding alcohol to such solutions we may often precipitate stable tetrammine salts, such as the sulfate, $Cu(NH_3)_4SO_4 \cdot H_2O$ (deep blue crystals). Observe that four molecules of ammonia here replace four molecules of water, which are similarly coordinated with a central cupric cation in ordinary cupric sulfate pentahydrate.

Cuprous ion also forms stable tetrammine salts. With both valences of copper the four ammonia molecules are all in one plane, at the four corners of a square, with the copper ion at the center.

Copper, in both valences, forms complex anions with chlorides and cyanides. This is doubtless the reason why cupric chloride is green rather than blue, especially in the presence of an excess of chloride. Cuprous chloride, though insoluble in water, readily dissolves in concentrated hydrochloric acid or in cyanides, forming the complex anions $CuCl_2^-$ and $Cu(CN)_2^-$. (Ex. 6, 7.)

568. Color Among Inorganic Compounds

Copper and gold are the only two colored metals. Colored ions are common among the transition metals but among the elements in the right-hand part of the Periodic Table colored ions are limited to gold

and cupric copper. It seems reasonable that colored ions owe their color to the oscillation of electrons between an outer group of electrons and an incomplete or easily disrupted inner group of nearly the same energy. That copper and gold possess colored salts is evidence that very little energy is needed to remove 1 or 2 electrons from the outer group of 18 that is present in cuprous or aurous salts (Cu^+, Au^+). This conclusion is supported not only by variable valence but also by the fact that copper, in an electric arc, shows two distinct series of spectral lines.

Color, among insoluble solid inorganic compounds, such as the oxides of lead, zinc oxide (at high temperatures), mercuric iodide, and the red form of mercuric sulfide, is obviously due to some peculiarity in crystal structure, for it often appears suddenly at some definite temperature. Moreover the color disappears when such compounds are dissolved in acid. Electrons within the crystal doubtless find two different distributions representing very nearly equal amounts of energy. By absorbing radiant energy of certain wavelengths they acquire energy to oscillate between these two levels. The substance then shows the color complementary to that represented by the wavelengths absorbed.

569. Silver and Gold

Silver is often found native (uncombined), in association with gold. Nevertheless its most important source is the small amounts of silver sulfide that accompany most ores of copper and lead. The world's annual production of silver is about 10,000 tons. About half of this is obtained from anode mud, a by-product of the electrolytic refining of copper (§ 522). Almost as much silver is recovered from lead reduced from ores that happen to contain small quantities of silver. Metallic zinc, stirred into the molten lead, rises to the surface, carrying most of the silver with it. The zinc may then be skimmed off and distilled, leaving the silver behind. This is the famous *Parkes process* for the recovery of silver.

The most important properties of silver are its *freedom from rusting, high luster, malleability*, and *ductility*. It has been beaten out so thin that several hundred sheets would be needed to make a layer the thickness of a leaf of this book; and the silver in a dime, if drawn into wire, could be made to extend more than a mile.

These properties of silver, together with its resistance to most acids and its freedom from rusting, make it useful for coinage, the manufacture of jewelry, and in decoration. Silver plating, the manufacture of

mirrors, and the photographic arts call for further large quantities. Nevertheless its uses, in comparison with cheaper metals, such as nickel and copper, are very limited—though they have not prevented the United States treasury from accumulating thousands of tons of it, at nearly twice its proper cost, in advance of any idea of what to do with it. The most promising suggestion is in the recent discovery (1939) that 5 pounds of silver, added to each ton of stainless steel, greatly improves the resistance of the steel to corrosion by sea water.

In silver plating, silver is deposited from a solution containing the complex argenticyanide ion, $Ag(CN)_2^-$, made by adding an excess of cyanide to a solution of a soluble silver salt. Although silver is here in an anion it is deposited at the cathode, doubtless because the complex anion is in equilibrium with a small concentration of silver ion, Ag^+. (Ex. 8, 9.)

In silvering glass, silver has usually been reduced from a solution in which it was present as an ammine salt, $Ag(NH_3)_2^+$, by the action of a slow reducing agent, such as glucose. The latest development is the production of mirrors by spraying, the silver solution and a quick-acting reducing agent being brought together at the nozzle of a spray gun. Reduction is accomplished in the instant that it takes for the sprayed particles to reach the surface to be coated.

Large quantities of silver are used in the preparation of photographic films and papers. The film itself is cellulose nitrate or acetate (§ 467). This is coated with an "emulsion" (really a *suspension*) of finely divided crystalline silver bromide, with a small amount of silver iodide, in the presence of a little gelatin. When light falls, momentarily, upon such a film a few silver ions, Ag^+, on each crystal are reduced to metallic silver, each perhaps demanding a quantum of radiant energy. Then when the exposed film is placed in a "developer" (usually an organic reducing agent), silver ions adjacent to the silver atoms already deposited are gradually reduced, until a large proportion of the silver halide crystals are partially or completely converted into metallic silver. From the negative thus obtained, one or more positive prints may be prepared by printing on paper (usually coated with a much more slowly acting emulsion than that used on the film).

Silver is usually univalent, but bivalent and tervalent complex silver salts are known.

Gold is often found free as grains or nuggets, in alluvial sand; but most of the gold now produced is attracted from the ore by chlorine or by sodium cyanide in the presence of air. Metallic gold does not rust or tarnish and does not dissolve in individual acids (except in

selenic acid). It does dissolve in solutions containing the free halogens, and for this reason is dissolved by aqua regia (in which the active agent is chlorine). The solution of the metal in aqua regia is doubtless assisted by the fact that it passes into solution as a complex ion, chloroaurate ion, $AuCl_4^-$.

In the extraction of gold from its ores by treatment with sodium cyanide in the presence of air, gold is oxidized to the tervalent condition and passes into solution as the complex auricyanide ion, $Au(CN)_4^-$, while the oxygen of the air is reduced to hydroxyl ion. The purpose of the cyanide is evidently to further the reaction by removing Au^{+++} from the solution as fast as formed (Principle of Mass Action, §§ 338, 426).

Gold forms halides in the valence states +1 and +3. Yet very few salts are known in which it is present as a cation. Its most important compounds are those in which it forms part of an anion, as in potassium aurate, $K(AuO_2)$; potassium chloroaurate, $K(AuCl_4)$; potassium aurocyanide, $K[Au(CN)_2]$; and potassium auricyanide, $K[Au(CN)_4]$. The two salts last mentioned are used in gold-plating baths. (Ex. 10–12.)

570. Zinc, Cadmium, and Mercury

Zinc is found chiefly as the sulfide, sphalerite, ZnS, usually in association with lead sulfide. The ore is roasted to remove sulfur and arsenic. The oxide thus formed may be reduced to impure zinc (often called spelter) by being heated with powdered coal. Or the ore may be incompletely roasted, to obtain a mixture of sulfate and oxide, which is extracted with sulfuric acid. The zinc sulfate solution so obtained may be freed from impurities by treatment with lime (which precipitates iron) and powdered zinc (which displaces and so precipitates the elements that fall below zinc in the electrochemical series). Manganese is best removed by bubbling a current of air through the solution, thus precipitating the manganese as the dioxide. After the precipitated impurities have been separated the purified solution is electrolyzed, zinc being deposited on an aluminum cathode.

2B
At. no. 30
Zn
48
Cd
80
Hg

Electrolytic zinc, prepared as just described, is about 99.9 per cent pure. Zinc alloys, including brass (§ 498), are usually prepared from electrolytic zinc, since impurities often seriously decrease their strength or otherwise injure them.

Metallic zinc is fairly malleable and ductile when heated to 100° to 150°C, but above 200°C it becomes even more brittle than it is

at room temperature. It is chiefly used as a protective coating for other metals, especially iron (§ 506).

Zinc oxide is a white paint pigment, also used in giving a white color to rubber. Zinc sulfate is used as a mordant in dyeing cotton fabrics. Treated with a solution of barium sulfide it yields a mixture of finely divided barium sulfate and zinc sulfide. This mixture is a permanent white paint pigment called *lithopone*. (Ex. 13.)

Zinc is bivalent in all its compounds. The hydroxide, $Zn(OH)_2$, is readily dissolved by alkalies, hence functions as a very weak acid. The product is a zincate, such as sodium zincate, Na_2ZnO_2:

$$Zn(OH)_2 + 2OH^- \rightarrow ZnO_2^{--} + 2H_2O$$

In acid solutions, by contrast, zinc hydroxide functions as a *base*, being dissolved to form a zinc salt

$$Zn(OH)_2 + 2H^+ \rightarrow Zn^{++} + 2H_2O$$

Since zinc hydroxide may either accept or lose protons it is classed as amphiprotic. The same is true of hydrous aluminum oxide, $Al(OH)_3$, and (less definitely) of hydrous chromic oxide, and the hydrous oxides of several other common heavy metals. *All zinc salts are poisonous.*

Cadmium usually accompanies zinc in zinc ores. It is similar to zinc in its chemical reactions, being bivalent in all its compounds. It is less reactive than zinc, hence makes a better coating for other metals, on which it is deposited by electrodeposition (for indoor applications) or by spraying the molten metal (inner coating of gasoline storage tanks). Cadmium with 1 or 2 per cent silver or nickel makes an alloy that is widely used for automobile bearings. It has a higher melting point than its nearest competitor, Babbitt metal.

Mercury is found in nature as the red mineral *cinnabar*, HgS, and occasionally as droplets of the free metal. When the ore is crushed and concentrated it needs only to be heated in a current of air to yield the free metal (and sulfur dioxide).

Mercury is the only metal that is liquid at room temperature. Its vapor and the salts of mercury are particularly dangerous poisons since they accumulate in the body with repeated small doses and finally bring disaster. Mercury salts should never be poured into the laboratory sinks, since they readily yield metallic mercury, which forms an alloy with metallic lead and so may ruin the plumbing.

Metallic mercury forms a few useful alloys (amalgams) and is used in the metallic state in thermometers, barometers, and pressure gauges. Mercury vapor has been used as a substitute for steam, in a few small

plants. Its advantage is that higher temperatures may be reached, hence higher efficiency obtained, without developing inconveniently high pressures.

Metallic mercury combines with mercuric ion, Hg^{++}, to form the peculiar diatomic ion, Hg_2^{++}, mercurous ion, characteristic of mercurous salts. Its formation is still unexplained. Otherwise, all three metals of this family would have an invariable valence of +2.

The most important of the compounds of mercury are mercurous chloride (calomel, Hg_2Cl_2), which is very slightly soluble, hence relatively non-poisonous, and mercuric chloride (*corrosive sublimate*, $HgCl_2$), which is readily soluble and violently poisonous. Mercuric sulfide is often produced as a white precipitate, which gradually turns black. When heated it becomes a bright red (the artists' pigment *vermilion*). (Ex. 14.)

571. Gallium, Indium, and Thallium

Gallium occurs as an impurity in zinc ores. It is a soft metal, which tarnishes readily and melts at summer temperature (30.8°C). Its bivalent compounds resemble those of zinc and its tervalent compounds those of aluminum. It has no important uses.

Indium also occurs as an impurity in zinc ores. It is also found in traces in ores of a number of the heavy metals, being readily detected in these by a pair of bright blue lines in its flame or spark spectrum. It is tervalent in most of its compounds, but may be reduced to the univalent or bivalent condition by vigorous reducing agents. It is readily obtainable in the refining of zinc, but is still without industrial uses.

	3A
At. no.	31 Ga
	49 In
	81 Tl

Thallium is much more abundant than gallium and indium and is recovered in considerable quantities from the flue dust of zinc retorts. It is a bluish white, easily tarnishable metal, which forms compounds in the valence states +1 (thallous compounds) and +3 (thallic compounds). These closely resemble the corresponding alkali metal and aluminum compounds. Thallous hydroxide, for example, is a caustic alkali. Thallium is used in a few alloys, and its compounds are sometimes added to optical glass to increase the index of refraction. Thallous sulfate, Tl_2SO_4, is used as poison for insects and rodents.

572. Germanium, Tin, and Lead

Germanium is of interest as one of the three elements whose properties and important compounds were predicted by Mendeleev in 1871,

some years in advance of their discovery (§ 214). It is recovered in the refining of zinc, and a few deposits of germanium minerals are known, from which the metal itself may be obtained by reduction of the oxide with carbon or by heating the oxide in a stream of hydrogen. Metallic germanium has a brilliant luster and is unusually resistant to acids.

Germanium has the chemical properties of a non-metal. Its halides, for example, are readily and completely hydrolyzed, and its chief compounds, the germanates, with the *anion* GeO_4^{----}, are analogous to the orthosilicates. Its oxides, GeO and GeO_2, are analogous to the two oxides of carbon or of silicon.

	4A
At. no.	32
	Ge
	50
	Sn
	82
	Pb

Tin occurs chiefly as the dioxide (cassiterite, SnO_2), a heavy mineral which appears in pockets in certain river beds, chiefly in the Malay States and in the Dutch East Indies. The tin ore, first concentrated by washing away or by frothing away the lighter particles, then is roasted, and leached with acid to remove acid-soluble impurities. The purified tin dioxide, thus obtained, may be reduced to metal by being heated with carbon. It is refined by cautiously oxidizing impurities that still remain, or by electrolysis in a bath of fluosilicic and sulfuric acids.

The most important use for tin is in coating sheet iron (§ 506). The coated iron sheets (tin plates) are chiefly used in the manufacture of tin cans. "*Block tin*" is solid tin, used for tubing for the distribution of distilled water. Tin foil has been almost displaced as a wrapping material by aluminum foil, waxed paper, Pliofilm, and cellophane.

Tin compounds display the valence states +2 and +4, corresponding to the oxides SnO and SnO_2. The hydrous oxides, like zinc hydroxide, are amphiprotic. The dioxide, dispersed in glass, results in an opaque enamel, used for coating metal in the preparation of sinks, bathtubs, stoves, and kitchen cabinets.

The stannous salts, Sn^{++}, are important reducing agents, being oxidized to the stannic condition, Sn^{+4}, by most oxidizing agents. Both stannous and stannic salts are readily hydrolyzed, hence cannot be long retained in solution except in the presence of an excess of acid. Solutions of stannous salts are, moreover, always kept in contact with metallic tin, which serves to reduce to the stannous condition any material that may become oxidized to the stannic condition by the oxygen of the air. Stannic salts are volatile covalent compounds—evidence, again, that it is impossible actually to form a cation, Sn^{++++}, with a quadruple positive charge.

Sodium stannate, Na_2SnO_3, is used for fireproofing fabrics. The cloth is soaked in a solution of this salt, then treated with ammonium sulfate solution, which precipitates metastannic acid (formed by hydrolysis) in the fibers. Silk is similarly treated to increase its weight.

Lead chiefly occurs as the sulfide (galena, PbS). This is concentrated, often by froth flotation (§ 507), then smelted by a very simple process, which begins with partial or complete roasting (to remove sulfur and arsenic) and ends with reduction by carbon (or by sulfur still remaining as PbS). Silica, usually present in the ore as an impurity, is slagged off as calcium silicate. Crude lead is often purified by electrodeposition from a solution of lead fluosilicate, $PbSiF_6$, containing fluosilicic acid and a little glue.

Lead is a soft metal, quickly tarnished in the air, but not deeply corroded by moist air, under ordinary conditions. It becomes plastic at about 300°C, hence may be extruded through a ring-shaped hole to form tubing, and may even be "wiped on" with a rag, in forming joints between sections of lead pipe. Its low melting point and resistance to dilute sulfuric acid have given it many industrial uses. Its important alloys include solder, type metal, and marine babbitt metal (§ 499). *All soluble lead salts are poisonous.*

Lead, like tin, forms two series of salts, in the valence states +2 and +4. Its oxides, like those of tin, are amphiprotic. In the higher valence state, +4, it forms volatile covalent compounds, such as lead tetrachloride, $PbCl_4$, and lead tetraethyl, $(C_2H_5)_4Pb$, and enters the anion in plumbates (Ca_2PbO_4, for example). In the lower valence state, +2, lead forms many important salts such as the nitrate, sulfate, acetate, and chromate, all of which have important industrial uses. A hydroxycarbonate [*white lead*, $Pb_3(OH)_2(CO_3)_2$] is still the world's most important white paint pigment, though it has recently had to compete with zinc oxide, lithopone (§ 570), titanium dioxide, and other substances. Its chief disadvantage is that it gradually darkens on exposure to the air, owing to the action of traces of hydrogen sulfide, which gradually convert it into lead sulfide (black). (Ex. 15, 16.)

Exercises

1. Write an equation to show what happens when pyrite is roasted, in a current of air, iron being oxidized to the ferric condition.
2. Write equations for the oxidation of copper matte in a Bessemer converter, the products being metallic copper, ferrous silicate, and sulfur dioxide.
3. Why is it important to reduce any cuprous oxide that may have been formed in oxidizing copper matte in a Bessemer converter?

4. What is α-brass? How does it differ in its properties from some other types of brass?

5. A dilute cupric solution is treated with an excess of iodide. The iodine set free requires 50 ml of $0.1N$ thiosulfate solution, in titration. To how many milliliters of $0.1N$ iodine solution does this correspond? What actual weight of iodine is this? What weight of Cu^{++} was present in the original solution? 635, 318

6. Write an equation for dissolving cuprous chloride in hydrochloric acid to form a complex acid with copper in the anion.

7. Write ionic equations for precipitating copper as cuprous cyanide from a cuprous solution, then redissolving the precipitate in an excess of cyanide.

8. Write an ionic equation to show how a silver salt may be converted into a complex salt, with silver in the anion, by adding an excess of cyanide.

9. What statement in the text indicates that the equation just written is reversible?

10. Write ionic equations showing how gold in each of its two principal valences may be converted into a complex cyanide, with gold in the anion.

11. Write an equation to show how gold is dissolved by a cyanide, in the presence of air.

12. Write and balance an equation to account for the presence of chlorine in aqua regia. Then show how chlorine and hydrochloric acid, acting together, dissolve gold to form chloroauric acid.

13. Write an equation for the preparation of lithopone.

14. Explain how metallic mercury, in contact with a solution of a mercurous salt, is able to prevent the oxidation of the salt to the mercuric condition, by contact with air.

15. Account for the fact that lead is rapidly corroded by acetic acid, in the preparation of white lead, but resists dilute sulfuric acid, when serving as chamber linings in the manufacture of sulfuric acid.

16. In the purification of lead by electrolysis, which common metals should accumulate in the anode mud and which ones should dissolve and accumulate in the solution?

Chapter 42

NUCLEAR CHEMISTRY

573. Radioactive Disintegration

Ordinary chemistry is concerned with events in the outer part of the *electronic system* that surrounds every atom. The formation of ions involves the transfer of one or more of the outermost electrons from one atom to another. The formation of molecules is accomplished by linking atoms together, through electrons that are shared between them. Such "ordinary chemical reactions" leave the deeper-lying electrons and especially the nucleus of the atom quite unaltered. So ordinary chemical reactions never convert one element into another.

But the decomposition of radium (§ 224) and other radioactive elements is quite another matter. *The rate at which radioactive elements decompose is unaffected by a change in temperature or by the presence of other elements in combination with the radioactive element.* This seems to indicate that radioactivity has nothing to do with the system of electrons in the external part of an atom. The *unstable (radioactive) atoms must possess unstable nuclei.* (Ex. 1.)

Events of an unknown sort within this nucleus now and then result in the nucleus being decomposed and an alpha particle (a helium nucleus) or a beta particle (an electron) being flung off. What remains is an atom of another element, which in its own turn may decompose. The final product in the disintegration of uranium, actinium or thorium is invariably an atom of lead.

Radioactive elements that disintegrate very rapidly are merely those whose individual atoms possess nuclei that are very likely to fall into an unstable condition and decompose within a short period of time.

574. Radioactive Sequences

When a radium salt is dissolved in water, and air is bubbled through the solution, the air carries away *a radioactive gas,* at first called *radium emanation,* but later found to be a new element, formerly termed niton, then renamed *radon* (Rn). The stream of air, rendered

radioactive by the radon it carries, may be passed through a plug of cotton (to remove solid and liquid particles), thence through a red-hot tube, and through powerful oxidizing or reducing agents, without losing its capacity for discharging an electroscope. *Radon is thus proved to be a chemically inert gas*, allied to helium, argon, and the other inert monatomic gases of the atmosphere (§ 355). Sir William Ramsay (1911) actually succeeded in weighing a sample of this gas, having a volume much smaller than the head of a pin, then calculated the weight of 22.4 liters (§ 116), and so was able to establish the *molecular weight* of radon. It turned out to be 222.

Radium continuously generates radon. It is also easy to prove that it continuously generates helium, as already described (§ 227). Assuming that the radium atoms are unstable, and disintegrate, one by one, ejecting doubly positively charged helium atoms (alpha particles), we may represent the disintegration thus:

$$\text{Mass numbers: } {}^{226}\,\text{Ra} \rightarrow {}^{4}\,\text{He} + {}^{222}\,\text{Rn}$$

The *atomic weights* of radium and helium being respectively 226 and 4, that of radon must be 222, identical with its molecular weight, as determined by Ramsay (§ 578). In other words, radon, like the other inert gases, has but one atom in a molecule. (Ex. 2.)

A sample of radon gas is found to become less and less active in discharging an electroscope, as time goes by. After a few days or a few weeks, depending on the amount of radon originally present, its activity is no longer detectable. At that time, however, the walls of the tube in which the radon has been kept are found to be radioactive. (Ex. 3.)

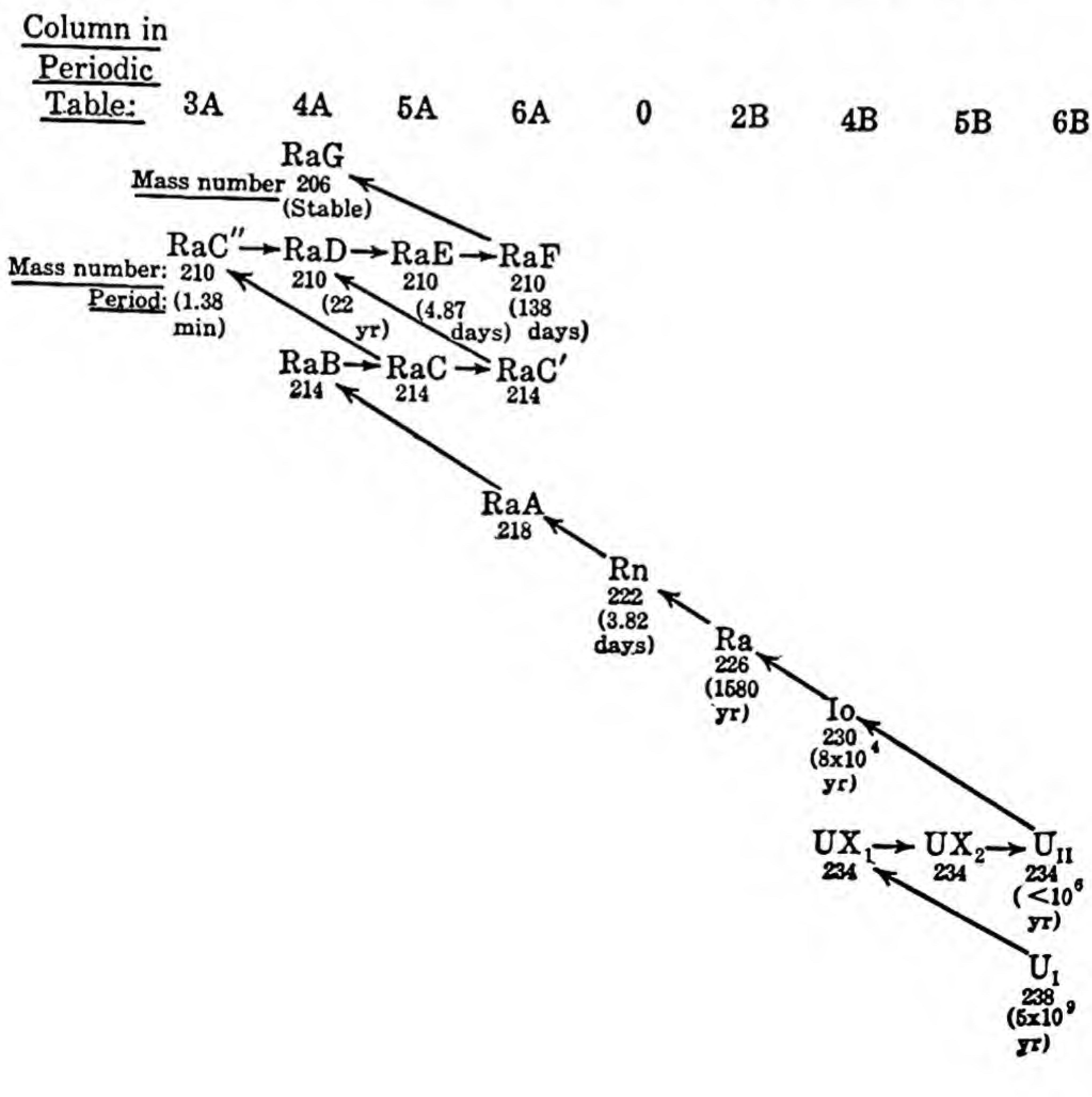
Evidently the atoms of radon are themselves unstable, and disintegrate, one by one, producing still simpler atoms. These decompose, in their own turn, in a definite *radioactive sequence*. Since radium is always present in uranium minerals, and nearly always in a definite ratio (1:3,000,000) to the weight of uranium present, it seems evident that radium is itself a product of the disintegration of atoms of uranium. Two decades of research, beginning with the work of Madame Curie, gradually convinced everyone that the loss of particles by unstable atoms occurs in a succession of miniature "explosions," in each of which *either* an alpha or a beta particle is ejected.

575. Radioactive Isotopes

When an alpha particle is emitted by a radioactive atom, in the sequences just considered, it carries a positive charge with it and hence

leaves a negatively charged residue. But this residue is an *atom of a metallic element*, hence cannot retain a negative charge, but on the contrary readily loses some of its external electrons and so assumes a positive charge. In brief, the heavy "residue particles," more commonly called *recoil atoms*, recoiling from the emission of alpha particles, are *positively charged metallic ions*, each having a particle weight four units less than the radioactive atom from which it came. These positive ions, if produced in the midst of a gas, can readily be collected on a negatively charged wire and a study made of their subsequent disintegration.

Something now turns up that is important and startling: *All the particles listed in any one column of the following diagram are merely different isotopes of the same element, namely, forms of the element that differ in particle weight but are chemically indistinguishable.* Thus in column 4A we find atoms of relative weights 206, 210, 214. They are called radium G, radium D, radium B, etc., as if they were different elements, but they are really only different isotopes of a single element,



which happens to be lead. Still other isotopes of lead are produced in the two other chief disintegration series, not shown in our diagram, which begin respectively with thorium and with a uranium isotope of relative mass 235.[1]

The times given in this table are those needed for *half* of any original quantity of a radioactive element to disappear (§ 579). (Ex. 4.)

576. Chemical Properties of the Radioactive Elements

The successive products of radioactive decay have been subjected to thorough chemical examination, for their radioactive nature permits them to be followed with an electroscope or particle-counter through the most complex chemical transformations, even when present in far less than visible traces. Let us reproduce here the last two lines of the Periodic Table:

3A	4A	5A	6A	7A	8A or 0	1A	2A	3B	4B	5B	6B
$_{49}$In	$_{50}$Sn	$_{51}$Sb	$_{52}$Te	$_{53}$I	$_{54}$Xe	$_{55}$Cs	$_{56}$Ba	Lanthanide elements (Rare earths) 57–71	$_{72}$Hf	$_{73}$Ta	$_{74}$W
$_{81}$Tl	$_{82}$Pb	$_{83}$Bi	$_{84}$Po*	$_{85}$?*	$_{86}$Rn*	$_{87}$?*	$_{88}$Ra*	Actinide elements* 89–96			

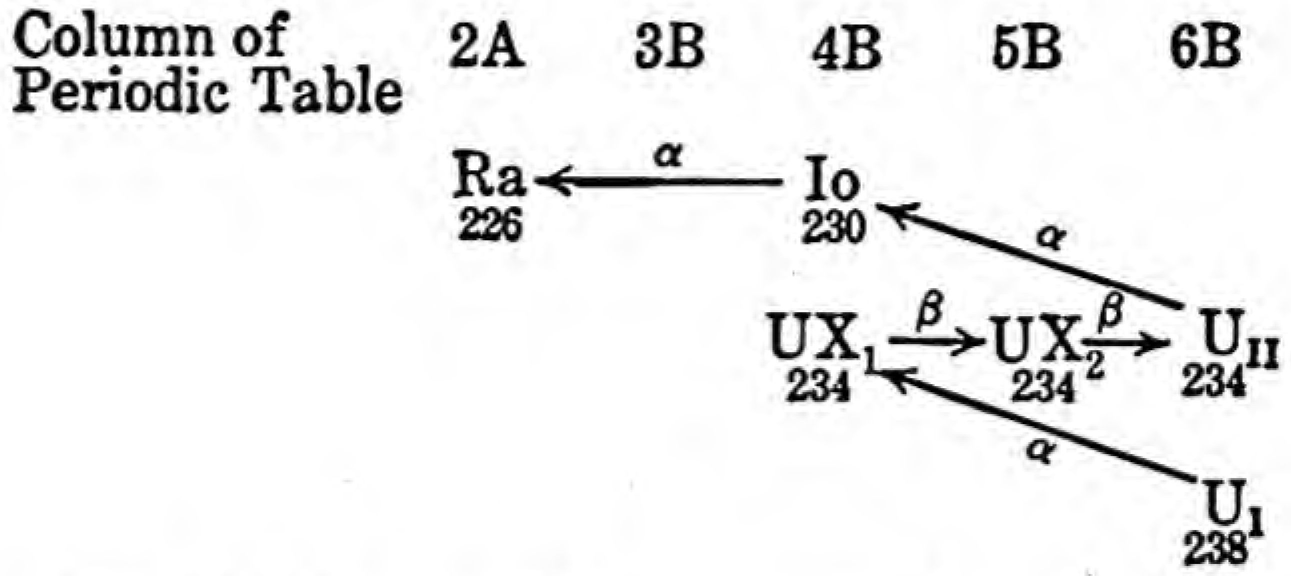
The elements marked with stars are known only as radioactive (unstable) isotopes. *Polonium* (Po) closely resembles tellurium in forming a gaseous hydride and an addition compound with carbon monoxide, analogous to TeCO. *Radon* (Rn) (or its isotopic variants, thoron and actinon) is a radioactive inert gas.

Radium is a metal closely resembling barium in the compounds that it forms and the solubility of its salts (§ 288).

577. Radioactivity and the Periodic Table

Let us now examine a portion of the diagram of p. 686—just enough of it to show the products obtained in the first few steps of the disintegration of an atom of uranium:

[1] The first three products in the disintegration of this isotope are uranium-Y, protoactinium, and actinium: $^{235}_{92}\text{U} \xrightarrow[\alpha]{} {}^{231}_{90}\text{UY} \xrightarrow[\beta]{} {}^{231}_{91}\text{Pa} \xrightarrow[\alpha]{} {}^{227}_{89}\text{Ac}$.



Since an expelled alpha particle presumably comes from the nucleus of the radioactive atom, and carries two positive charges with it, we seem justified in concluding that the new atom produced by the loss of an alpha particle has had the positive charge on its nucleus *decreased by two units.* But the new atom, produced by the loss of an alpha particle, always occupies a position two places toward the left of the original atom, in the Periodic Table. (Ex. 5.)

By contrast, the loss of a beta particle (unit negative charge) gives the nucleus a unit *increase* of positive charge, and carries the element forward one place in the Periodic Table. This confirms a conclusion already drawn (§ 231) from the deflection of alpha particles, in passing through thin sheets of metal: *Each step forward in the Periodic Table adds unit positive charge to the nucleus of an atom and one electron to the outer part of the atom.* (Ex. 6.)

578. Another Way to Deduce Avogadro's Number

If a small sample of radioactive material is placed at a distance *r* from a zinc sulfide screen or near the window of the ionization chamber (§ 226) we may count the number of particles that arrive at the screen or window during any given period of time. But the radioactive material meanwhile has been hurling off alpha particles in all directions, indiscriminately. So, comparing the area of the screen or window (*A*, Fig. 182) with the total surface of a sphere of radius *r*, we may calculate the total number of alpha particles hurled off by the radioactive sample in all directions, during any given period of time.

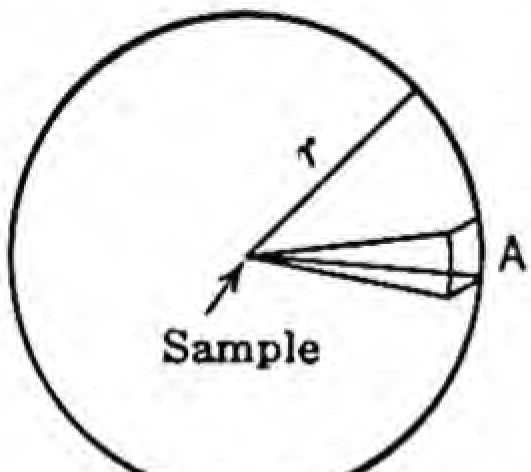


FIG. 182.

It turns out that 1 mg of radium (in equilibrium with the short-lived elements that arise from it and are always associated with it) emits 4.35×10^{15} alpha particles, He^{++}, each year. These alpha particles presently lose their charges and become atoms of ordinary helium. Ramsey and Soddy collected and measured the helium gas set free by a small sample of radium during a very long period. It

amounted to 0.158 cu mm ($= 0.158 \times 10^{-6}$ liter) of helium under standard conditions, per milligram of radium per year. This much helium came from the 4.35×10^{15} alpha particles.

Now let us calculate how many alpha particles, that is, how many atoms (or *molecules* [2]) of helium are needed to produce one *mole* of helium, namely, 22.4 liters of helium gas, under standard conditions:

$$\frac{22.4}{0.158 \times 10^{-6}} \times (4.35 \times 10^{15}) = 616 \times 10^{21} = 6.16 \times 10^{23}$$

molecules of helium in one mole of helium. But a mole of any substance is a weight of material that is large or small in proportion to the molecular weight. If a mole of helium contains 6.16×10^{23} molecules of helium, then a mole of any other substance must contain the same number of molecules (Avogadro's number). Observe how closely the number thus derived agrees with its value as deduced from Millikan's determination of the charge of an electron (§ 176). (Ex. 7.)

579. The Reversed Compound Interest Law

We cannot prophesy the future fate or length of life of an individual atom any more than we can that of an individual human being. But uncounted millions of atoms are present in every sample of radioactive material; hence definite *average* figures can be given. We can determine the *average life* of an individual atom and what is called the *period* or *half-disintegration period* of the element, namely, the time that it will take for half of the element to decompose—just as tables compiled by life insurance companies give us the average expectancy of life of a person of any specified age, and the number of years that must elapse before half of any age group will have passed from the earth.

The rate at which a radioactive element disintegrates is proportional to the amount that still remains. This *Law of Radioactive Disintegration* is actually a "reversed compound interest law." A sum of money in the bank will double itself at compound interest after a definite number of years, depending upon the rate of interest. A radioactive substance, on the contrary, will be reduced to half its original quantity after a definite half-disintegration period. For radium, the half-disintegration period is 1580 years, corresponding to depreciation at the rate of about $\frac{1}{22}$ per cent, compounded annually. Worse investments have been known. (Ex. 8.)

[2] A molecule of helium contains only one atom.

580. Long-Lived and Short-Lived Elements

The half-disintegration period of a radioactive element may occasionally be determined directly by noting the time required for the radioactivity to decrease to half its original value.

The half-disintegration period of *radium* has been determined by observing how many alpha particles are emitted by a gram atom of radium in a year, then comparing this result with Avogadro's number.

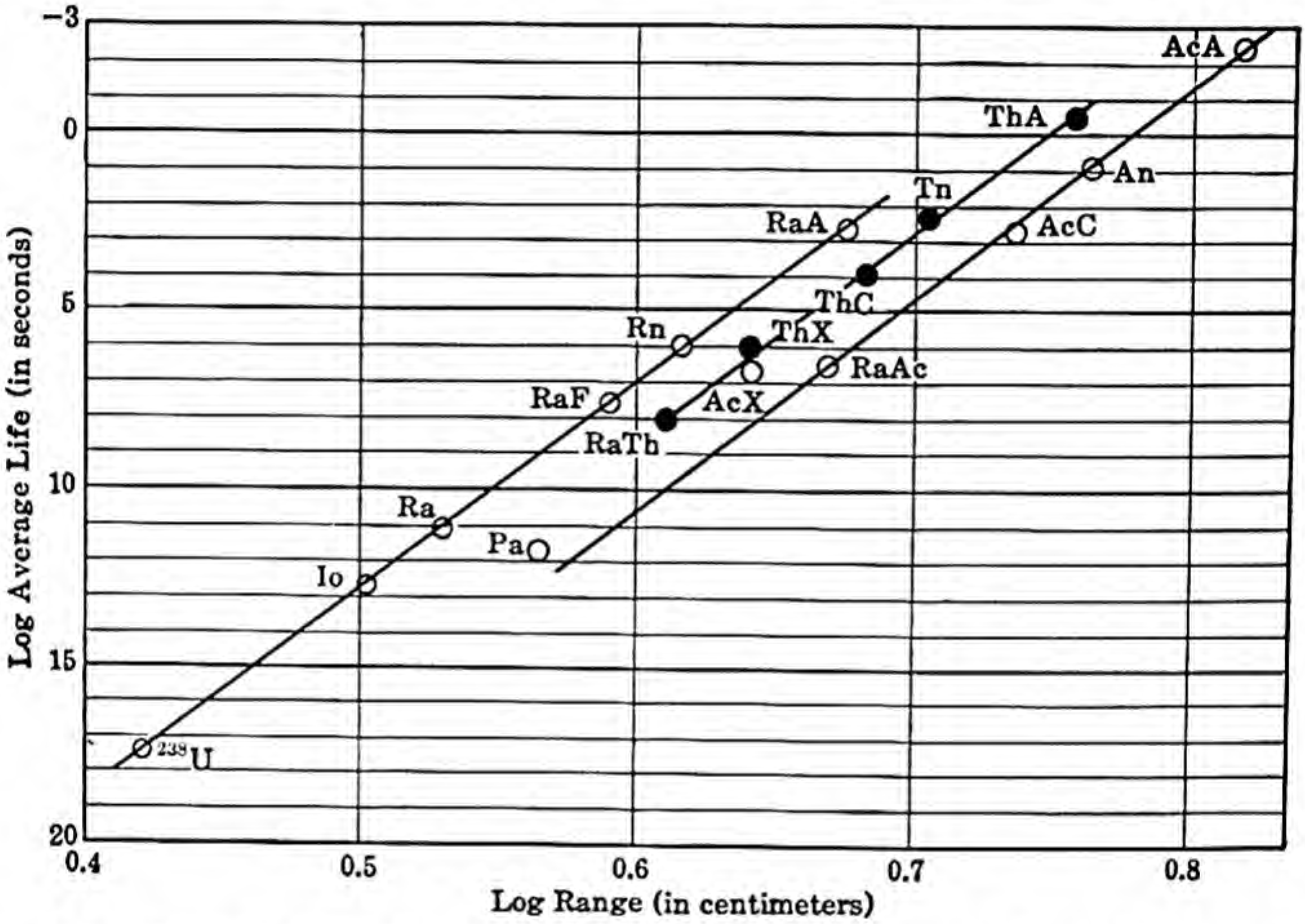


FIG. 183. Geiger-Nuttall Law. The logarithm of the range of an alpha particle, in each of the three chief radioactive sequences, is very nearly *linearly related* to the logarithm of the average life.

Thus estimated, the half-disintegration period of radium turns out to be 1580 years.

With a long-lived element, such as uranium or thorium, the half-disintegration period has to be obtained indirectly. We notice that uranium minerals that have not been exposed to leaching always contain 2.86×10^6 atoms of uranium for every atom of radium. We infer that a *steady state* has been reached, in which uranium is being converted into radium at the same rate as radium is being converted into other radioactive products. This could be possible only if uranium had a half-disintegration period 2.86×10^6 times as long as that of radium, that is, one of $2.86 \times 10^6 \times 1580 = 4.52 \times 10^9$ years.

The half-disintegration period of very short-lived alpha-particle emitters is obtained by determining the range of the alpha particles.

The shorter the life of an atom the more violently it expels an alpha particle and the greater the range of the particle (Fig. 183).

The longest-lived radioactive element turns out to be thorium, with a half-disintegration period of 1.6×10^{10} years (16 thousand million years). The shortest-lived element thus far discovered is thorium C, with a half-disintegration period of a hundred thousand millionth of a second (10^{-11} sec). (Ex. 9.)

581. Radioactivity among the Lighter Elements

The unstable atoms thus far mentioned are those of the heavier elements, from thallium (atomic number, $Z = 81$) to uranium ($Z = 92$), near the end of the Periodic Table. This suggests that atoms of elements beyond uranium are completely unstable and short-lived, and hence do not exist in nature.

Among the lighter elements, *potassium* and *rubidium* are faintly radioactive, emitting beta rays of very low penetrating power (half-disintegration periods are respectively 10^{12} and 10^{11} years). These rays almost certainly come from the presence in these two alkali metals of traces of unstable isotopes of masses 40 and 86:

$$^{40}\mathrm{K} \xrightarrow{\beta} {}^{40}\mathrm{Ca} \qquad\qquad {}^{86}\mathrm{Rb} \xrightarrow{\beta} {}^{86}\mathrm{Sr}$$

Samarium, among the rare earths, emits fairly penetrating alpha rays, and one or two other rare-earth elements seem to have barely detectable alpha-ray activity. So the atoms of certain isotopes of these light elements are unstable, and the mere *heaviness* of atoms of uranium, thorium, radium, etc., is not the cause of their lack of stability.

► 582. Radioactivity and the Age of the Earth

Since the disintegration of uranium and thorium liberates helium and at length produces lead, careful chemical analysis of a mineral to determine the ratio of uranium or thorium to helium or lead will enable us to estimate the period of time that has elapsed since the formation of the mineral. Of course, the age of a mineral, estimated from its content of helium, tends to be too small, since the mineral is rarely dense and impervious enough to retain all the helium gas that is produced within it. Estimated from the content of lead, the age tends to be too large, since the lead may not all have been of radioactive origin. From the uranium-helium ratio, phosphatic sharks' teeth, from comparatively recent (Pliocene) geological strata, have been found to be around a hundred thousand years old. Minerals from Devonian strata (the Age of Fishes) are about 350 million years old.

The early (Pre-Cambrian) rocks, which underlie and antedate the earliest fossil records, are from 1000 to 1500 million years old.

These estimates are in reasonable agreement with estimates based on rates of deposition and erosion of geologic strata. The earth has been wheeling through space for quite a long time.

583. Rutherford's Experiment

An English physicist, Ernest Rutherford (1919), discovered that alpha particles from radium C, in traversing ordinary nitrogen gas, produced a long-range *secondary radiation*, which proved to consist of swift-moving, positively charged hydrogen atoms, in other words, *protons*. These could not have come from hydrogen or water vapor contained as an impurity in the nitrogen traversed, for they possessed a greater range than was ever observed for protons produced in that way. Moreover, they were projected in all directions, even toward the point from which the alpha particles came.

All this seemed to indicate that these long-range protons were propelled by a sort of explosion, produced when a speeding alpha particle collided with the nucleus of a nitrogen atom. A second product of the disruption of the nitrogen nucleus was later shown to be a *new variety of oxygen*, with a particle weight of 17. Thus the transformation may be represented:

$$\begin{array}{l} \text{Mass numbers:} \\ \text{Atomic numbers:} \end{array} \quad \underset{\text{Nitrogen atom}}{{}^{14}_{7}\text{N}} + \underset{\text{Alpha particle}}{{}^{4}_{2}\text{He}} \rightarrow \underset{\text{Proton}}{{}^{1}_{1}\text{H}} + \underset{\text{Oxygen atom}}{{}^{17}_{8}\text{O}} + \text{Kinetic energy}$$

Such symbols refer to nuclei rather than to complete atoms. Each *superscript numeral* (small figure at a higher level than the line of type) gives the mass (to the nearest whole number) of the nucleus concerned; each *subscript numeral* (small figure at a lower level) gives the *atomic number*, namely, the nuclear charge.

In such transformations *both mass and nuclear charge must be conserved:* On the left-hand side of the equation we have a total mass number of 18 and total nuclear charge of $+9$; the same totals must be found on the right-hand side. Our equation emphasizes that the transformation of a nitrogen nucleus, under the impact of an alpha particle, releases a large quantity of energy, which takes the form of kinetic energy of the ejected proton and the newly formed oxygen atom. Only thus may we account for the extreme range of the proton. (Ex. 10.)

Rutherford's experiment was the first well-established instance of the artificial transmutation (conversion) of one element into another.

It produced oxygen from two simpler elements, nitrogen and helium. Incidentally, it showed that not only alpha and beta particles but also sometimes *protons* might arise from the decomposition of the nucleus of an unstable atom.

584. Projectiles and Projectile Accelerators

Rutherford's experiment suggested using alpha particles from radium or any other radioactive material as "projectiles" to "bombard" the nuclei of different elements in an attempt to transmute them into other elements. Unfortunately, one cannot aim the projectiles toward the nuclei which it is desired to shatter. Hardly one projectile in ten million actually encounters a nucleus; the rest simply dissipate their energy in ionizing atoms near which they happen to pass. Shattering atomic nuclei by any method thus far conceived is a little like trying to kill game in a not very thickly inhabited forest by random shots in the dark. Nevertheless, with the aid of alpha particles, many other instances of the transmutation of elements were discovered during the 20 years immediately following the work of Rutherford. (Ex. 11.)

Alpha particles emerge from radioactive material with a very high velocity (a consequence of the strong repulsion between the positively charged nucleus of the radioactive atom and the positively charged alpha particle that it releases). A disadvantage is that any ordinary quantity of radioactive material will not release very many alpha particles during the course of any experiment. (Ex. 12.)

So other projectiles came into use. Special equipment was invented to give protons and deuterons (the ionized form of heavy hydrogen, § 96) sufficient velocity to enable them to shatter nuclei. Sometimes these "projectile accelerators" took the form of a high voltage transformer or an electrostatic generator (up to 100 million volts). Still more famous is the cyclotron (Fig. 184). This consists of a giant

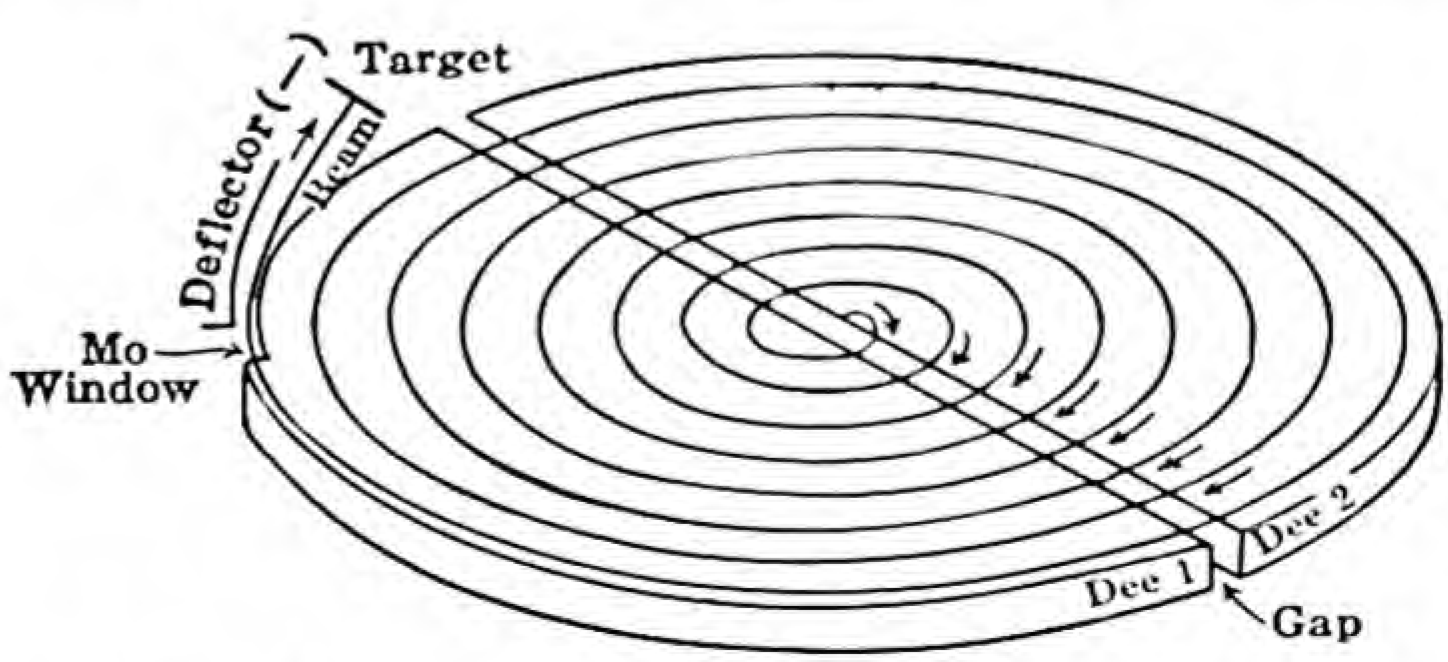


FIG. 184. Path of the particles in a cyclotron.

electromagnet, between the poles of which is interposed a hollow flat disk, within which positively charged particles (protons or deuterons) are accelerated as they travel a spiral path in a nearly complete vacuum, until they attain velocities of thousands of miles a second.

One such instrument, housed in an underground laboratory at the University of California, gives protons or deuterons with kinetic energy equivalent to that gained by an electron in traversing an electrostatic field of 16 million volts. Deuterons emerging from this cyclotron have sufficient velocity to penetrate 5 feet of ordinary air. Another will presently be completed to yield deuterons at 200 million electron volts (defined, p. 709), and capable of penetrating 100 feet of ordinary air; or protons or alpha particles at 400 million electron volts.

By more recent devices (the *betatron* and *synchrotron*) even electrons have been given sufficient velocity to enable them to be used as atom-shattering projectiles.

585. The Neutron

The greatest discovery in the field of nuclear physics during the interval between the two great world wars was the discovery of the neutron by the British physicist Chadwick, in 1934. Neutrons are particles with a mass just perceptibly greater than that of a proton. But the neutron is electrically neutral (has a zero nuclear charge), hence is represented by ${}^{1}_{0}n$. Chadwick produced neutrons by the bombardment of beryllium with alpha particles, the equation being

$${}^{9}_{4}\text{Be} + {}^{4}_{2}\text{He} \rightarrow {}^{12}_{6}\text{C} + {}^{1}_{0}n$$

So all one needs to produce neutrons in large numbers is a small sample of a radium salt, mixed with beryllium powder! (Ex. 13.)

Other important ways of producing neutrons are by the bombardment of deuterium atoms with deuterons (from a cyclotron), the bombardment of lithium atoms with deuterons, and the interaction of deuterium with gamma radiation.

Atoms of many different sorts emit neutrons when bombarded by projectiles. So neutrons seem to be a fundamental component of matter. The nucleus of every atom is assumed to contain enough protons to account for the nuclear charge; whereas the total mass of the nucleus is accounted for by protons plus neutrons:

$$\text{Number of protons in nucleus} = Z \text{ (nuclear charge)}$$

$$\text{Number of protons} + \text{number of neutrons} = M \text{ (mass number)}$$

With the exception of hydrogen and a rare isotope of helium, there are at least as many neutrons as protons in the nucleus of every atom. For the heavier elements, the number of neutrons always exceeds and sometimes considerably exceeds the number of protons.

The function of the neutrons in the nucleus is evidently to overcome the repulsive force that exists between the protons. In some manner, not yet explained, the neutrons prevent the nucleus from flying apart under the influence of the mutual repulsion of the protons contained in it. This ability of neutrons to hold protons together in a compact nucleus is limited to very small distances (of the general order of 10^{-12} cm).

A disadvantage of positively charged particles (alpha particles, protons, or deuterons), as projectiles in atom-shattering experiments, is that they are strongly repelled by the positively charged nuclei which they are intended to collide with and shatter. As a positively charged projectile approaches a strongly positively charged nucleus (*i.e.* a nucleus of any element toward the end of the periodic system) the latter, in most instances, wards off the blow! But neutrons, being uncharged, are not repelled by the "target" nuclei. Indeed, any neutron that happens to pass very close to a nucleus may actually be attracted by the latter. (Ex. 14.)

So *neutrons make almost ideal projectiles in atom-shattering experiments.* Almost their only disadvantage is that (being electrically neutral) they cannot be accelerated by being passed through an electrostatic field. One must be content to use them at velocities determined by those with which they emerge from the nuclei of beryllium and other elements. This velocity is usually sufficient, indeed is often too great: Neutrons need to be slowed down by passage through graphite or through a hydrocarbon, such as paraffin (from which they eject protons) if they are to react effectively with the nuclei of uranium and some other elements. If they move too swiftly they seem to by-pass the target nuclei or to pass right through them, without producing any permanent alteration! (Ex. 15.)

586. Positrons and Mesotrons

In 1933 the "positive electron" or *positron* was discovered as an incident to the investigation of *cosmic rays* (mysterious penetrating radiation which reaches our earth from outer space). Cosmic rays seem to be a very complicated phenomenon, in which high-frequency radiant energy and high-speed electrons are intermingled with the products of disintegration of atomic nuclei. The positron has an

almost negligible mass (that of the electron) and a charge which is the same as that of an electron except that it is positive instead of negative. (Ex. 16.)

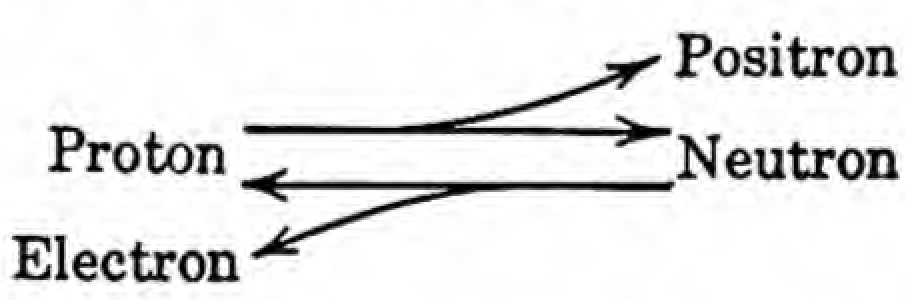
Nevertheless, *in ordinary chemical experience*, positrons are never encountered. Positively charged particles, whenever observed in electric discharges through gases or in chemical experimentation, have turned out to have an enormous mass, relative to the electron, and so have been recognized as positively charged material particles, namely, as positively charged ions (cations).

Here, then, is a fundamental difference between negative and positive electricity. Negative electricity is readily divorced from matter and then takes the form of nearly massless electrons. Positive electricity, by contrast, clings to matter so tenaciously that we ordinarily observe it only in the form of positively charged material particles (cations), though atom-shattering blasts of concentrated energy, delivered by cosmic rays or otherwise, may now and then free positive electricity as nearly massless positrons. These, within a very brief fraction of a second, pass out of existence by reacting with the electrons of ordinary matter, their combined energy being released as radiant energy:

$$e^+ + e^- \rightarrow h\nu, \text{ otherwise written } {}^0_1e + {}^{\ 0}_{-1}e \rightarrow h\nu$$

if we take note of the charges and approximate masses of the two "particles."

Observations of artificially radioactive substances (§ 587) indicate that the proton and the neutron are probably interconvertible. The proton, by loss of a positron, may become a neutron. The neutron, by loss of an electron, may become a proton:



The question of the internal structure of atoms has been made more complicated by the discovery (in investigations of cosmic rays, 1938) of the *mesotron*, which is a particle having the same charge as an electron, but *extra mass* (two hundred times the mass of an electron) which is of course interpreted as extra energy. Their existence is exceedingly brief, perhaps for a millionth of a second. Then they are resolved into ordinary electrons and radiant energy:

$$\text{Mesotron} \rightarrow e + h\nu$$

587. Artificial Radioactivity

Bombarding atoms often results in unstable atoms that sometimes emit *positrons* and sometimes *electrons*. The first observations were made by Irene Curie-Joliot, daughter of the discoverer of radium, with her husband, F. Joliot. For this discovery they received the Nobel prize in physics, for 1934.

Whether electrons or positrons are emitted in any particular case of artificially induced radioactivity is shown in a very striking manner in Fig. 185. The stable isotopes of the first few elements are represented by black circles, and known radioactive isotopes by open circles, marked + or − according as they lose positrons or electrons in reverting to a stable condition. Whenever the ratio of mass number (M) to atomic number (Z) is *too great* for stability, atomic number is increased by 1 unit in a radioactive change in which the nucleus loses an *electron;* in the contrary case, in which an atom possesses *too low* a ratio of mass number to atomic number, the atomic number is decreased by 1 unit in a radioactive change in which the nucleus loses a positron, or (less commonly) captures an electron from the innermost (K) group of electrons, or (rarely) loses an alpha particle.

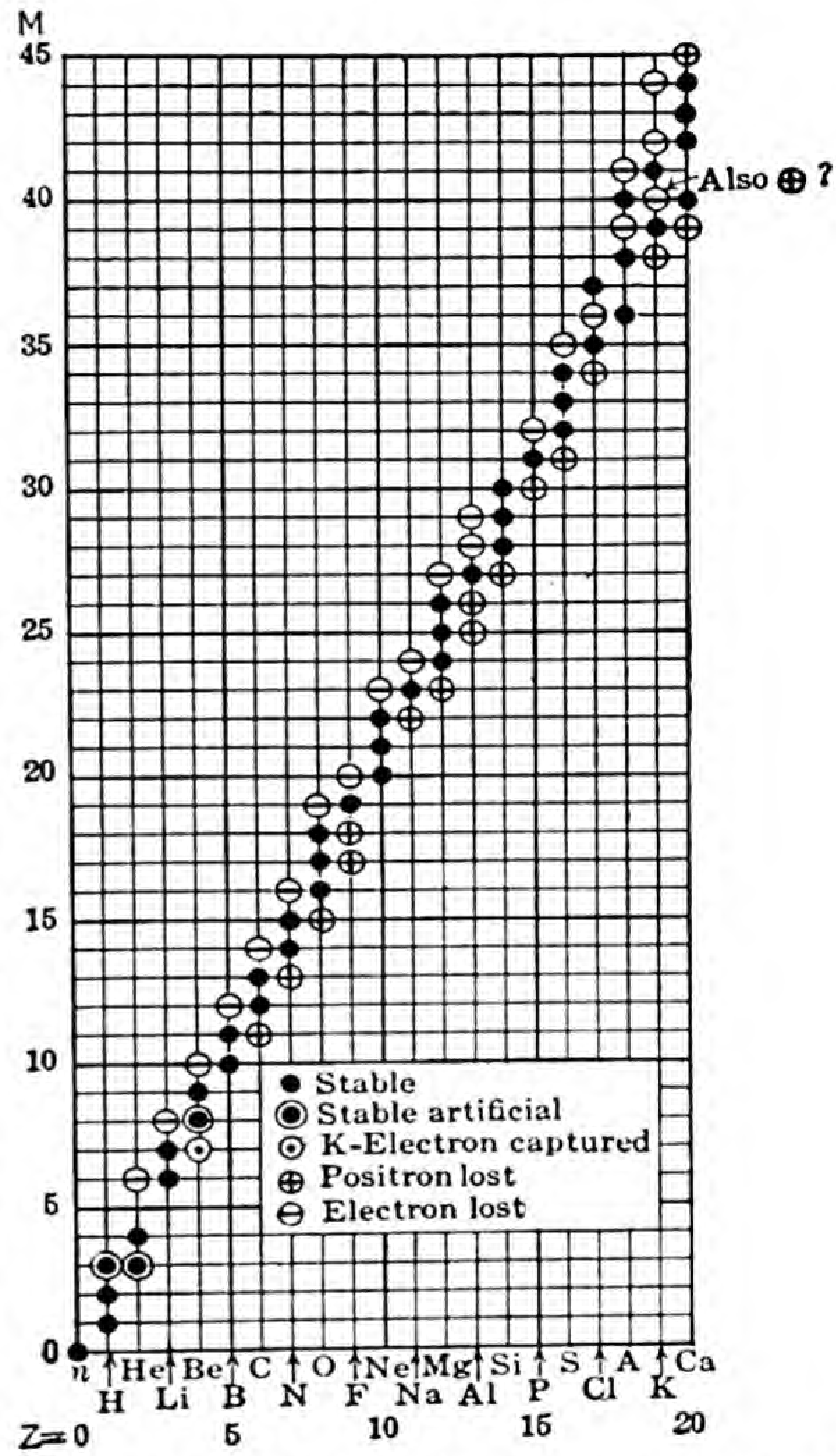


FIG. 185. Stable and unstable isotopes of the first twenty elements.

An interesting triumph is the conversion of ordinary bismuth, ^{209}Bi, into radioactive bismuth, ^{210}Bi, by bombardment with neutrons. The unstable bismuth thus produced turns out to be identical with the naturally occurring radioactive element *radium E* (§ 575): It has the same half-life period (5 days), emits beta particles (electrons), and produces a product, radium F (polonium), which emits alpha

particles having the same range as those emitted by polonium of natural origin. This is the first instance of the artificial creation of one of the radioactive substances found in nature. (Ex. 17.)

588. Tracer Atoms

Of the more than thirty naturally occurring radioactive types of atoms now known, the great majority have never been obtained in visible or weighable quantities. Yet their chemical properties have been studied, in some instances in great detail. The electroscope, like a bloodhound's nose, can smell out mere traces of the radioactive elements in any sort of hiding place. Thanks to the marvelous sensitivity of this instrument, a few hundred atoms of any intensely radioactive element may be detected and identified with certainty. A sensitive analytical balance, by contrast, is barely affected by the weight of about 10^{18} atoms (the number expressed by a 1 followed by eighteen zeros)!

Three of the ordinary elements have radioactive isotopes that may be used as "tracer atoms," to keep track of the fate of larger samples of the non-radioactive isotopes of these elements. For example, radium B and thorium B are radioactive forms of lead; they differ from ordinary lead only in particle weight and in being radioactive. If atoms of these radioactive forms of lead are mixed with ordinary atoms of lead, they will follow the latter indefinitely, in whatever transformations, in their original proportions.

For example, small amounts of lead salts with a little thorium B have been injected intravenously into experimental animals, and traced in the various organs after a period of a few hours or a few days, by burning samples of the organs and testing the ash with an electroscope. Or an organ, being thus made radioactive, will record its image on a photographic plate with an intensity proportional to the amount of lead or bismuth that it contains. Thus it has been determined that lead is chiefly retained by the liver, and bismuth by the kidneys.

This very neat method for detecting mere traces of an element was at first available only for the three heavy metals (lead, bismuth, and thallium) that happen to possess radioactive duplicates. But most of the lighter elements may be rendered radioactive by artificial means (§ 587). This discovery now permits mere traces of these elements (calcium, nitrogen, and phosphorus, for example) to be followed through the mazes of chemical transformations in the animal body as easily as lead, thallium, and bismuth. We may learn, for example,

how long it takes calcium, obtained from an animal's food, to be deposited in its bones. This is a triumph worth celebrating. (Ex. 18.)

By employing a particle counter (§ 226) instead of an electroscope, *individual elements, in traces too small to be detected by spectroscope or electroscope, may now be followed through complex transformations, with comparative ease.* Thus the unstable atoms ${}^{13}_{7}N$ and ${}^{30}_{15}P$ have been proved definitely to be nitrogen and phosphorus, because their radioactivity is transferred from solid aluminum (target) to a gas under conditions that would have resulted in the formation of gaseous ammonia, NH_3, or gaseous phosphine, PH_3. We have plenty of evidence that a radioactive element remains radioactive when combined with other elements.

589. Classifying Nuclear Transformations

With the four different projectiles we have described, or by the use of high-frequency radiant energy, hundreds of different examples of nuclear transformations have been observed, and practically every element (in one or more isotopes) has been artificially produced. Altogether about 500 different unstable (artificially radioactive) types of atoms have been created, since the discovery of artificial radioactivity in 1933! In most instances, their mass numbers and nuclear charges have been determined.

Nuclear transformations are of about 25 well-defined classes, each of which is represented by a symbol which indicates the *projectile* used and the *light-weight product* that results from the collision of the projectile with the nucleus of another atom. Important examples:

Projectile	*Light-weight Product*	*Symbol for This Transformation Type*
Alpha particle	Proton or neutron	$(\alpha;\ p,\ n)$
Deuteron	Proton, neutron, or alpha particle	$(d;\ p,\ n,\ \alpha)$
Proton	Alpha particle or gamma rays; or none	$(p;\ \alpha,\ \gamma,\ -)$
Neutron	Proton, alpha particle; or none	$(n;\ p,\ \alpha,\ -)$
Gamma rays	Neutron	$(\gamma;\ n)$

Rutherford's experiment (§ 583), for example, would be formulated: ${}^{14}_{7}N(\alpha,\ p){}^{17}_{8}O$.

590. Weighing Energy

If we make an accurate accounting of mass, in nuclear transformations, to the fourth decimal place, we always find that the sum of the masses of the resultants is *slightly less* than the sum of the masses of

the reactants. Otherwise expressed, *in shattering the nucleus a small amount of mass always disappears.* As an example consider the bombardment of the less frequent lithium isotope, ${}^{6}_{3}Li$, with deuterons:

$$
\begin{array}{lccccc}
 & {}^{6}_{3}\mathrm{Li} & + \; {}^{2}_{1}\mathrm{H} & \rightarrow \; 2\,{}^{4}_{2}\mathrm{He} & + & \text{Kinetic energy} \\
\text{Accurate masses:} & 6.0168 & 2.0147 & 2 \times 4.0039 & & \begin{array}{c}0.0237 \text{ (missing)} \\ \text{("mass defect")}\end{array}
\end{array}
$$

The mass that here seems to disappear amounts to 0.0237 unit of atomic mass. The explanation is that the two helium atoms produced in the disintegration are flung off with considerable kinetic energy, and *energy possesses mass*, as Einstein long ago recognized (§ 69). (Ex. 19.)

The 0.0237 missing unit of mass, in the experiment just described,[3] corresponds to 22 million electron volts of energy. Dividing this energy between two alpha particles we find an energy of 11 million electron volts for each. An alpha particle of this energy should have a range of 13 cm in air. This checks observation almost exactly.

Conversely, from the ranges and hence the energies of the particles produced in a nuclear transformation, we may calculate the mass of any particle whose mass happens not to be known. Thus deuterium, under the influence of high-energy gamma rays, is broken down into protons and neutrons:

$$
\begin{array}{lcccccccc}
 & {}^{2}_{1}\mathrm{H} & + & {}^{0}_{0}\gamma & \rightarrow & {}^{1}_{1}\mathrm{H} & + & {}^{1}_{0}n & + \quad \text{Kinetic energy} \\
 & \text{Deuterium} & & \gamma \text{ rays} & & \text{Proton} & & \text{Neutron} & \\
\text{Masses:} & 2.0147 & + & 0.0028 & = & 1.0081 & + & ? & + \quad 0.0006 \\
 & & & \begin{array}{c}\text{(Calculated} \\ \text{from frequency)}\end{array} & & & & & \begin{array}{c}\text{(Calculated from range} \\ \text{of proton and neutron)}\end{array}
\end{array}
$$

Solving for the mass of the neutron, we find it to be 1.0088 units of mass, with a possible error of about 0.0005.

591. Nuclear Fission of U235

In 1934 the Italian physicist Fermi observed that uranium, when bombarded by slow neutrons, appeared to be converted into other elements. One of the products of this *nuclear reaction* was afterward (1939) identified as barium. Then American physicists, in collaboration with Fermi, then living in the United States, proved that only one of the three isotopes of uranium (and one not very plentiful) was affected by slow neutrons.

It was shown that the nucleus of this uranium isotope, U235 (namely ${}^{235}_{92}U$), when struck by a slow neutron, is split into two nearly equal particles, together with several neutrons, with the release of radiant energy, as suggested in Fig. 186. Here was an entirely new

[3] See footnote, p. 707.

phenomenon, *nuclear fission* (the splitting of a nucleus into two or more nearly equal parts, with the release of a large amount of energy). (Ex. 20.)

Actually, the U235 nucleus can be split in a great many different ways, each of which produces a heavy fragment with a mass in the range 127 to 154 and a somewhat lighter fragment with a mass in the range 83 to 115. *These fragments are radioactive.* By emission of one or more beta particles (electrons) they are gradually converted into stable elements. About 30 different elements (including barium, neon, and iodine) have been identified among these products of the decomposition of U235, each of the several most abundant of them constituting nearly 10 per cent of the total.

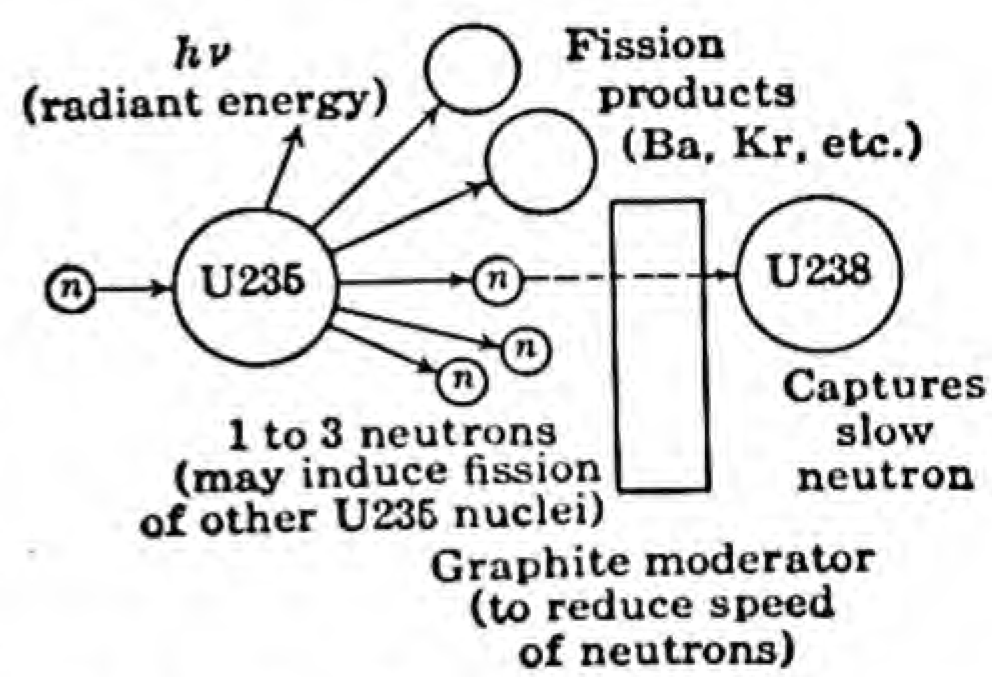


FIG. 186. Fission of a U235 atom by a slow neutron.

The fragments of the U235 nucleus fly off with very high velocities. The energy total released is about 200 million electron volts. Translated into more familiar figures, one pound of U235, in being converted into other elements by bombardment with slow neutrons, would yield 11.4 million kilowatt-hours of energy (roughly that obtainable by burning 1500 tons of coal or 200,000 gallons of gasoline)!

The most important fact about the fission of the U235 by slow neutrons is that *several new neutrons originate from every atom of U235 that is decomposed.* This suggested that it might be possible to set up a *chain reaction* (§ 333) in which a slow neutron decomposes an atom of U235, thus releasing several neutrons. These could be slowed down by passage through some hydrogen compound or through graphite, then used to decompose other U235 atoms—and so on, indefinitely! If this chain reaction were rapid enough it would result in an explosion, more devastating than any ever known before. A kilogram of U235, decomposed even to the extent of 5 per cent, would produce destruction equivalent to about 300 tons of TNT.

This chain reaction is the principle behind the dread atomic bomb. The chief difficulty in its development lay in the fact that the uranium isotope U235 makes up only about 0.7 per cent of the total weight of ordinary uranium. The remainder is a heavier isotope, U238, with a small trace of U234. Worse yet, the U238 absorbs neutrons without being fissioned, hence the proposed chain reaction might not go on in

its presence. So the possibility of an atomic bomb at first seemed to depend on separating the isotopes of uranium from one another. This is no easy matter, as we shall see.

592. Separation of Isotopes

The isotopes of an element are practically identical in chemical characteristics, hence cannot be separated by chemical reactions.[4] Separation must depend on any *physical properties* that happen to differ slightly from one isotope to another on account of the slight difference in mass.

The separation of the isotopes of *hydrogen* has been accomplished by repeated *fractional electrolysis*. When a considerable portion of a sample of ordinary water has been electrolyzed, the residue that remains contains much more than the normal proportion of the heavy isotope of hydrogen, deuterium (§ 96).

Recently, the separation of deuterium has been accomplished by taking advantage of the fact that when steam (and liquid water) is in equilibrium with hydrogen gas (in the presence of a catalyst) the water contains three or four times as high a proportion of deuterium as is contained in the hydrogen gas. This method depends on the discovery of good catalysts, which insure that the water and hydrogen shall be in chemical equilibrium at every moment. Water thus enriched in deuterium must be further enriched by repeating the operation many times, if nearly pure deuterium is finally to be obtained.

The separation of the isotopes of *neon* was first accomplished by repeated *fractional distillation*, with the aid of an efficient distilling column (§ 298).

None of the methods just described are effective for the separation of isotopes of *uranium*, hence other methods had to be perfected. One of these depends on the fact that *light molecules diffuse more rapidly through porous membranes than heavy molecules do.* This method must be applied to *gases* or *vapors*. The uranium compound chosen was UF_6, which is a solid that can be vaporized (sublimed) at 56°C. (Ex. 21.)

Comparing the masses of ${}^{235}_{92}UF_6$ and ${}^{238}_{92}UF_6$ and remembering that the rate of diffusion (§ 111) is inversely proportional to the square root of mass, we see that the lighter isotope should diffuse $\sqrt{352/349} = 1.004$ times as fast as the heavier one, if separation is attempted by the diffusion of UF_6 through a porous membrane.

[4] Hydrogen is an exception, since the percentage difference in the masses of its isotopes is unusually great.

This obviously assumes that all the molecules of any given mass have the same velocity, which of course is not true (§ 113). So the separation of isotopes by diffusion of a gaseous compound through a membrane is actually very difficult, and requires repeated passes of the gas through a porous membrane.

To separate a few grams daily of U235 from the abundant isotope, U238, and obtain it perhaps 95 per cent pure, would require many acres of diffusing membrane and thousands of passes of every intermediate portion of the gas through the membrane. Special membranes had to be invented containing billions of openings in every square meter, no openings with a larger diameter than 10^{-6} cm. Special pumps—and thousands of them—had to be installed to recirculate the intermediate fractions of the gas in the plant that was built at Oak Ridge, Tennessee.

Material thus very much enriched in U235 was subjected to an electrostatic separation, based on an elaboration and improvement of the mass spectrograph, described in § 35. In this way, nearly pure U235 was finally obtained in considerable quantities.

593. Creating Plutonium from Uranium

In separating and investigating the rare uranium isotope (U235) it was discovered that the more abundant isotope, U238, is capable of *capturing* neutrons, to produce a new radioactive isotope, U239:

$$^{238}_{92}\mathrm{U} + {}^{1}_{0}n \rightarrow {}^{239}_{92}\mathrm{U} + \underset{\text{Radiant energy}}{h\nu}$$

The U239 is soon converted (by loss of an electron) into a new element, *neptunium*, atomic number 93. This in turn loses an electron and is converted into still another new element, *plutonium*, atomic number 94:

$$^{239}_{92}\mathrm{U} \rightarrow \underset{\text{Neptunium}}{^{239}_{93}\mathrm{Np}} + \underset{\text{Electron}}{_{-1}^{\ 0}e}$$

$$^{239}_{93}\mathrm{Np} \rightarrow \underset{\text{Plutonium}}{^{239}_{94}\mathrm{Pu}} + {}_{-1}^{\ 0}e$$

The half-disintegration periods for the two radioactive transformations here indicated are respectively 23 minutes and 2.3 days. The names uranium, neptunium, and plutonium for the three elements at the end of the periodic system are appropriately derived from the names from the three planets in the outermost part of the solar system.

Plutonium itself proved to be capable of fission when bombarded with neutrons, hence was an alternative material for the possible

construction of an atomic bomb. It had the advantage over U235 in being chemically distinct from uranium, hence in being separable by chemical processes rather than by the tedious physical methods needed for the separation of isotopes.

To create plutonium from uranium on a large scale, one would need to intermingle ordinary uranium with some "moderator," capable of slowing down neutrons. Then, on subjecting the mixture to neutrons from some outside source, one might hope to find the U235 in the uranium to be decomposed, liberating neutrons, some of which would be used in converting U238 into plutonium, leaving others to be slowed down by the moderator, then to decompose new atoms of U235, in a chain reaction.

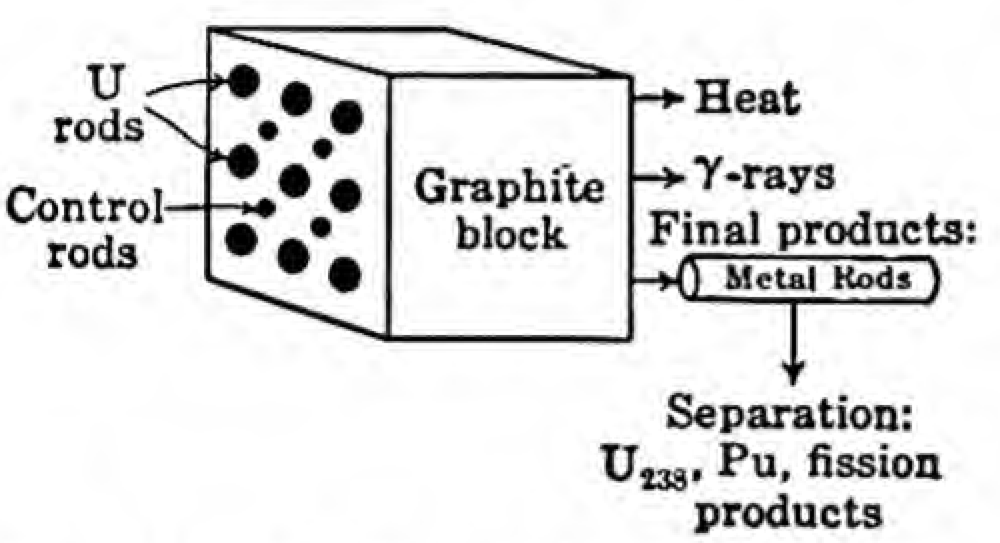


Fig. 187. Principle of a "pile" for converting uranium into plutonium and radioactive fission products.

To reason clearly about such a process one ought to realize that there are several concurrent processes, one producing, the others absorbing, neutrons:

1. The production of neutrons by the fission of U235 nuclei.

2. The disappearance of neutrons in converting U238 into plutonium, or in being captured by the nuclei of elements present as impurities, or by escaping into the air.

The first process must produce enough neutrons to keep the others going; but must produce no more than barely enough, if the reaction is to be kept under control. The balance between the opposing processes depends on the sizes of the intermingled particles of uranium and moderator, on their relative amounts, on the nature and amount of impurities, on the temperature, on the surface exposed to the air, and of course on the proportions in which U235 and U238 are present in the uranium.

As actually carried out, the process was somewhat as summarized in Fig. 187. A cubical "pile" of highly purified graphite contained openings into which cylinders of highly purified uranium, sealed in aluminum cans, could be introduced. Other openings, not shown in the figure, contained control rods of neutron-absorbing material, such as boron steel or cadmium, which could slow down the reaction by being pushed deeper into the pile. The pile was usually cooled by circulating water.

The chain reaction began spontaneously (from stray neutrons or

from cosmic rays) when the pile had been built up to a certain *critical size* (in other words to a certain ratio of volume to surface). When purified metallic uranium of the normal isotopic composition was used, with purified graphite as a moderator, about six tons of uranium needed to be present in the pile, before the chain reaction started. Thereafter the reaction proceeded spontaneously during weeks and months, while the minor isotope, U235, was gradually converted into radioactive fission products, together with neutrons, and the major isotope, U238, was gradually converted into plutonium. The pile meanwhile yielded energy (chiefly as heat, delivered to the cooling water), often at the rate of several hundred kilowatts. After a time the fission products from the U235 had accumulated in sufficient quantities to absorb an undue proportion of the neutrons emitted, hence the pile had to be shut down and the plutonium separated from the very large excess of uranium that still remained.

594. Plutonium, Americium, Curium

The final problem in the production of plutonium was to learn enough about its chemical properties to design a plant for its separation from uranium. Since it is radioactive its reactions could be followed (§ 588) with an electroscope or Geiger counter, when only invisible traces of the element were present. Then half a milligram was produced and (by specially devised *ultramicro techniques*) was made to disclose the chemical properties of plutonium in a sufficiently definite way to warrant investment of millions of dollars in plants for its separation.

Plutonium proved to be very similar to uranium in its chemical properties, as is disclosed by the fact that it exists in valence states +3, +4, +5, +6. Its separation from uranium was accomplished by dissolving the mixed metals in acid, precipitating the plutonium in the valence state +4 in the presence of a coprecipitated "carrier," followed by extraction and separation from the carrier by oxidation to the valence state +6. All these operations were carried out by remote control, from behind thick concrete walls, to protect operators against the penetrating radiations of the radioactive fission products of U235. Protection also had to be provided against poisoning by uranium or plutonium (a particularly dangerous poison because it is radioactive). There was also need for preventing risk of injury to the population or vegetation of the neighboring countryside from escape of radioactive gases, and for minimizing explosion risks in the operation of the piles. (Ex. 22.)

U235 and plutonium may be stored without risk of explosion as long as they are in small pieces. The fission of occasional atoms by stray neutrons or by cosmic rays then releases neutrons which for the most part escape harmlessly into the surrounding atmosphere. But when small pieces are merged into a single mass, above a certain critical mass, most of the neutrons liberated by the fission of any nucleus must collide with and decompose other nuclei before they reach the surface of the material. The result is a chain reaction or nuclear explosion.

The chemistry of neptunium could at first be studied only with samples of the very short-lived isotope $^{239}_{93}Np$. But another isotope, $^{237}_{93}Np$, has a period of 2.25×10^6 years, hence is more easily studied. It is a product of the emission of beta particles by $^{237}_{92}U$, and can also be produced synthetically by bombarding uranium with fast neutrons.

By the bombardment of $^{238}_{92}U$ and $^{239}_{94}Pu$ with high energy helium nuclei, generated in a cyclotron, two other synthetic elements have been created, with properties that show them to be closely related to uranium, neptunium, and plutonium. They have been termed *americium*, $_{95}Am$, and *curium*, $_{96}Cm$. So at present (1946) 96 elements are known, of which eight (43, 61, 85, 87, 93–96) were first identified and studied as synthetic isotopes, prepared from other elements. With perhaps one exception, they are probably too unstable (short-lived) to exist in nature.

595. Nuclear Energy

Everyone hopes that the splendid scientific work which led to the development of the atomic bomb may be made to serve mankind in times of peace. The known uranium deposits of the world probably contain enough U235 to furnish all the energy requirements of the United States for one or two centuries. But the question is still open whether nuclear energy from uranium can compete with other sources of energy in peacetime applications.

The most direct way to obtain some of the nuclear energy of uranium would be to operate the piles that convert U238 into plutonium at so high a temperature that the water now used to cool the piles would be converted into steam. This may or may not be possible. If further energy is sought in the fission of plutonium or U235 one would meet the problem of disposing of dangerous radioactive products. On the other hand, these products should have future applications in medicine and industry that may make them worth producing on their own account.

The most effective source of nuclear energy now known is U235, which is present in ordinary uranium in such a small proportion that piles designed to release its energy are cumbrously large and are very inefficient. Piles in which the uranium is "enriched" by the addition of extra U235 are smaller and more efficient, but U235 is now obtainable only by very expensive methods (§ 592). If produced at \$52,000 a pound, U235 would furnish energy equivalent to that obtained from gasoline at 20 cents a gallon; if produced for as little as \$18,000 a pound it might compete with coal at \$12 a ton. But other considerations, such as convenience, risk of explosion, or danger of corrosion or of poisoning, might outweigh the mere cost of energy. It seems probable that nuclear energy, released from uranium, will for a long time be able to compete with energy derived from ordinary sources (fuel and waterpower) only in very special uses, in which convenience and economy of space might outweigh extra cost.

Thorium, though not itself fissionable, is converted into the fissionable uranium isotope ^{233}U when exposed to neutron bombardment in a uranium pile. So thorium is of military interest. Protoactinium is fissionable, but too scarce to be important.

Some idea of the promise of different elements as sources of nuclear energy may be gained by comparing the total mass of the nucleus of any atom with the total mass of the protons and neutrons which are assumed (§ 585) to have been incorporated in that nucleus. *There is always a loss of mass in the creation of any nucleus from protons and neutrons.* This loss of mass is of course (§ 590) equivalent to the energy released in the formation of that particular kind of nucleus. It is also the energy that would need to be supplied to decompose the nucleus into protons and neutrons. It is called the *binding energy* of the nucleus. The higher the binding energy is, the more stable the nucleus.

For example, consider the nucleus of helium. Its mass is 4.0028 units. Compare this with the total mass of the two protons (2×1.00758) and two neutrons (2×1.00893) of which it is assumed to be composed. We see that this synthesis corresponds to a loss in mass of 0.030 unit, in binding the protons and neutrons together to form the helium nucleus. It corresponds to a binding energy [5] of

$$0.030 \times (1.49 \times 10^{-3}) \times (6.02 \times 10^{23}) = 2.7 \times 10^{9} \text{ ergs per mole}$$

This is the energy that would be released in synthesizing 1 mole (4 g) of helium from protons and neutrons.

[5] 1 mass unit (on the scale that makes $^{16}_{8}O = 16$) $= 9.31 \times 10^{8}$ electron volts $= 1.49 \times 10^{-3}$ erg $= 4.15 \times 10^{-17}$ kw-hr, for each nucleus or atom transformed.

In Fig. 188 we have roughly plotted the fractional binding energy for the chief isotopes of most of the elements. We see that it is highest for elements in the middle part of the Periodic Table. These are the most stable elements.

If any nuclear reaction is to yield energy, potential energy must decrease (§ 67) or its negative (binding energy) must increase. Figure 188 shows that there are several possibilities:

1. Energy would be released if we could synthesize middle-weight atoms from light atoms. This is doubtless the source of most of the energy liberated by the sun and stars.

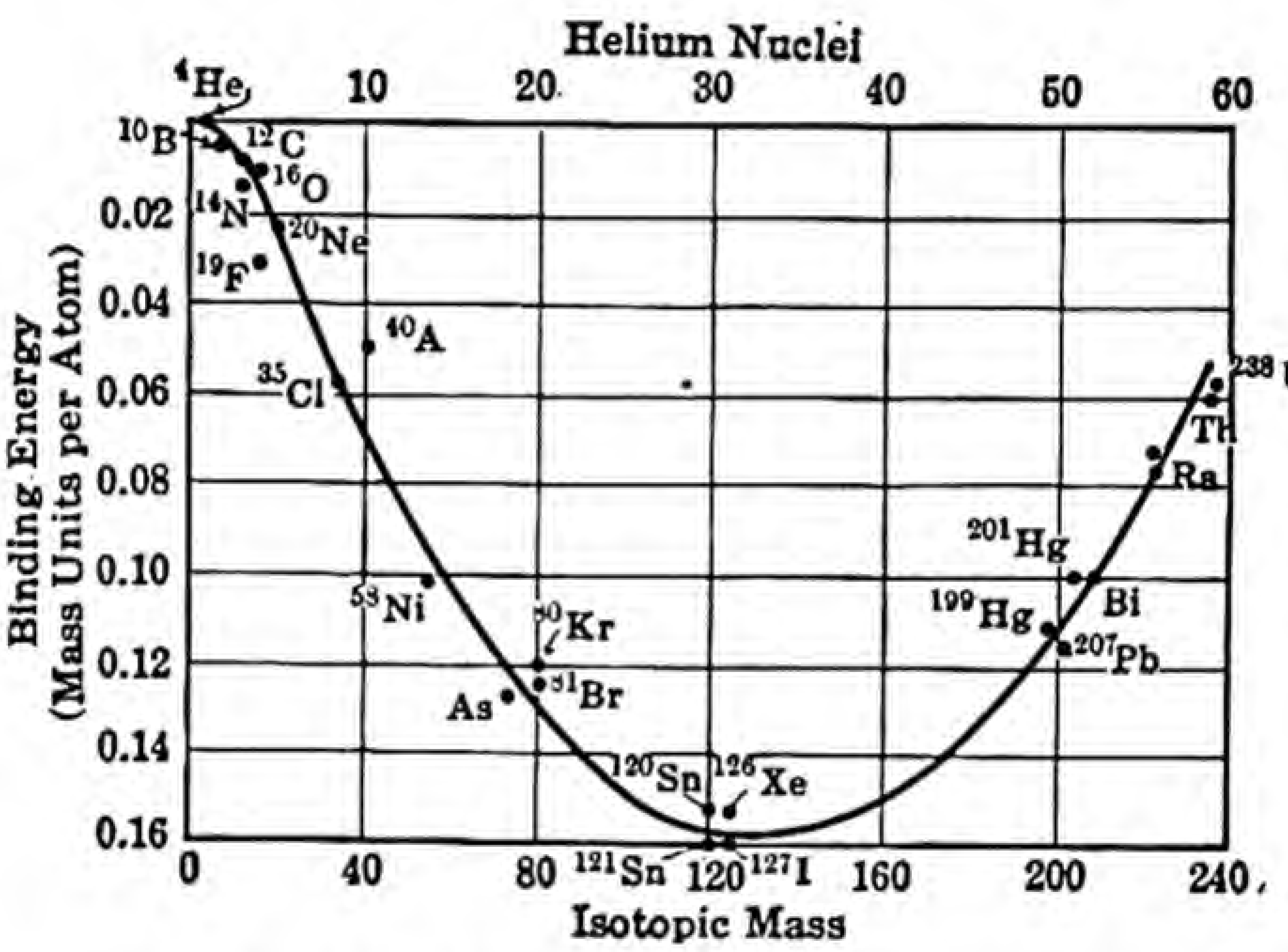


FIG. 188. Diagram showing that the most stable elements are those near the middle of the periodic table.

2. Some of the heavy atoms, toward the end of the Periodic Table, may be fissioned, with the production of middle-weight fragments. The fission of uranium and plutonium are examples.

3. A few isotopes of the light elements are unstable and may be decomposed by bombardment, releasing energy. (Ex. 23.)

A large part of production of energy by the sun is by some physicists believed to be due to a reaction in which carbon serves as a sort of nuclear catalyst for the conversion of hydrogen into helium:

$$^{12}_{6}C + {}^{1}_{1}H \rightarrow {}^{13}_{7}N \rightarrow {}^{13}_{6}C + \underset{\text{Positron}}{{}^{0}_{1}e}$$

$$^{13}_{6}C + {}^{1}_{1}H \rightarrow {}^{14}_{7}N$$

$$^{14}_{7}N + {}^{1}_{1}H \rightarrow {}^{15}_{8}O \rightarrow {}^{15}_{7}N + \underset{\text{Positron}}{{}^{0}_{1}e}$$

$$^{15}_{7}N + {}^{1}_{1}H \rightarrow {}^{12}_{6}C + {}^{4}_{2}He$$

Observe that the last step releases an atom of carbon, which can start a new cycle. The net result of the process is the disappearance of four protons in creating a helium nucleus and two positrons.

All the steps in this cycle have been observed in the laboratory, when carbon and nitrogen have been bombarded with protons. Until we have learned how to combine them or to combine similar nuclear reactions of other kinds into a self-sustaining cycle we cannot be said to have entered upon the Nuclear Age. [6]

Technical Words

Electron volt—the energy acquired by an electron or any other particle of unit charge in passing through an electrostatic field between plates having a difference of potential of one volt. One (absolute) electron volt equals 1.602×10^{-12} erg. If one electron volt of energy is released as radiant energy the frequency (§ 323) of the latter is 2.418×10^{14} per second. Larger energies, expressed in electron volts, when released as radiant energy, result in proportionately higher frequencies.

Emanation—a nearly obsolete term, originally used to designate any radioactive gas (radon, thoron, actinon).

Mass number—the mass of the nucleus of an atom, relative to $^{16}_{8}O = 16$, rounded to the nearest whole number.

Recoil atoms, p. 686. **Cyclotron,** p. 693. **Betatron,** p. 694.

Steady state (less properly called **radioactive equilibrium**), p. 690.

Period or **half-disintegration period,** p. 689.

Average life—the average time that must elapse before an atom of a radioactive element disintegrates. It is 1.44 times the half-disintegration period.

Deuteron (D^+ or $^2_1H^+$)—the ionized form of deuterium (§ 96).

Positron, p. 696. **Mesotron,** p. 696. **Nuclear fission,** p. 701.

Binding energy—the energy calculated (from loss of mass) to be released in the synthesis of a nucleus from protons and neutrons; it is numerically equal to the energy that would be needed to decompose the nucleus into protons and neutrons. It is usually expressed as the *fractional loss of mass* in the synthesis of a nucleus from protons and neutrons.

Exercises

1. What evidence indicates that it is the nucleus of an atom that is concerned in radioactive decomposition?
2. Write an equation for the radioactive decomposition of radium.
3. Why does the radioactivity of radon continuously decrease and finally become undetectable?
4. Look up the half-disintegration period of radium D in the table on p. 686, thence infer what part of the radioactivity of a sample of that element will remain after 110 years.
5. What change occurs in the mass of the nucleus and in the position of the residue in the Periodic Table as the result of the loss of an alpha particle?

[6] By many miscalled the Atomic Age, which is of course that of ordinary Synthetic Chemistry.

6. What change occurs in the mass of the nucleus and in the position of the residue in the Periodic Table, as the result of the loss of a beta particle?

7. Give a description of the manner in which Avogadro's number has been deduced by counting alpha particles.

8. Explain (p. 709) how the average life of the atoms of a radioactive element can be deduced from its period.

9. By what indirect method has the period or average life of very short-lived or very long-lived atoms been deduced?

10. Describe Rutherford's experiment and summarize it by an equation.

11. What three positively charged particles are commonly used as projectiles in bombarding the nuclei of atoms?

12. What disadvantage do alpha particles have as projectiles in comparison with projectiles accelerated by artificial means?

13. How were neutrons first produced? What are their chief characteristics in comparison with protons?

14. Why do neutrons make more promising projectiles in atom-shattering experiments than the positively charged particles previously employed?

15. What disadvantage do neutrons possess as atom-shattering projectiles?

16. Compare positrons with some other particles with respect to mass and charge.

17. How may some of the ordinary elements be made to exhibit artificial radioactivity? What two kinds of particles are emitted by most of the artificially radioactive elements?

18. What is meant by a tracer atom? Explain how tracer atoms may be used in determining the migration or deposition of some of the elements in the living body of an animal.

19. Who was responsible for the concept that matter and energy are interconvertible? What quantity of energy, expressed in ergs, comes from the disappearance of 1 gram of matter?

20. What is meant by nuclear fission? Which atom was the first to be fissioned?

21. What method has been successfully used for the separation of the isotopes of each of the following elements: hydrogen, neon, uranium?

22. Indicate the manner in which the most abundant isotope of uranium may be converted into plutonium. Summarize this conversion in an equation. Indicate the need for precautions against injury to workmen, in the separation of plutonium from the unchanged material at the end of the operation of a "pile."

23. By what two chief types of nuclear transformations, opposite in character, may atomic energy conceivably be released?

Chapter 43

CHEMISTRY AND THE SPIRIT OF SCIENCE

So here we are at the end of our attempt to sketch the general outlines of the science of chemistry, presented as a *manner of thinking*. The chemical facts with which we dealt have interested us chiefly as raw material in the interpretation of facts, through generalizations called *laws*, then through a few great *theories*, by which the laws themselves are interwoven and in some degree explained. Thus we have gained some insight into the methods by which science has won its advances.

596. The Collection of Facts

Every reader must have been impressed with the multitude of facts that need to be surveyed, even in an elementary course in chemistry. The course should be concluded by a visit to a chemical library, in which a few volumes of the great reference books, each comprising many volumes, are pulled from the shelves and peered into, in the fields of inorganic, organic, analytical, physiological, and industrial chemistry. Every page of these handbooks swarms with references to published researches in chemical periodicals. The newest of these periodicals have come into existence within the past few years; the oldest of them, filling whole shelves in the library, stretch back in unbroken sequence to the days of Priestley and Lavoisier, more than a century and a half ago. Here the chief languages of the world join in friendly rivalry in the diffusion of knowledge, using symbols and formulas whose meaning is understood in every land.

It is easy to perceive that the amateur observer in the fields of chemistry and physics has little hope of adding anything very significant to the mass of facts already known. The same is fast becoming true of the biological sciences. This is the age of specialists. Tens of thousands of professional investigators, in all the sciences, in every part of the world, are busily at work collecting new facts, which pour into the

hoppers of the great abstracting journals, in every science, in an ever-growing stream. *Chemical Abstracts*, an American journal, searching the chemical literature of the world for new contributions, in 1939 abstracted over 45,000 separate articles and 20,000 patents, dealing with chemistry and its applications, in 3200 different periodicals, published in 31 languages.

597. The Generalization of Facts into Laws

Yet facts, however numerous, never make a science. The scientific worker views facts as a means to understanding. He seeks first of all to classify data and so to arrive at general statements of facts. This is a process called *induction*.

Every law includes a multitude of facts that would otherwise need to be remembered separately. Every law, moreover, suggests new facts which might otherwise remain undiscovered. For example, a multitude of facts suggested the Periodic Law—that the ninety-odd elements, arranged in the order of increasing atomic number, display a rough periodicity in all their properties.

The numberless facts of every science are marshaled under a few great laws. These may at first be only rough approximations to the truth. Witness the Law of Dulong and Petit, formerly used as a means for inferring atomic weights (§ 146), though it gave results that were doubtful by at least 5 per cent. Sometimes a law is given a simple form by brushing aside all sorts of minor deviations and complications. Thus we invent such concepts as an ideal gas, an ideal crystal, or an ideal solution.

On the other hand, we discover a few laws that seem to hold true exactly, without the least deviation. The laws of Conservation of Mass and Conservation of Energy (or, better, their *joint* conservation, § 69) are good examples. So is Faraday's Law (§ 523) and the Law of Constant Composition (§ 24) for definite chemical compounds, if we take due account of isotopes. These are among the most important laws in the whole field of science. Of similar rank, in other sciences, are Newton's Laws of Motion, the Law of Gravitation, Coulomb's Electrostatic Law, and Mendel's Law of Inheritance.

598. The Development of Theories

Scientific laws weld what would otherwise be a bewildering multitude of disconnected facts into a few easily remembered general conclusions. Yet the more precisely stated or far-reaching a law becomes, the more it clamors for an explanation. Why should doubling the

pressure on a gas compress it to very nearly half its former volume? Why does heat disappear when the liquid vaporizes? Why should crystals tend to assume a symmetrical regular form, bounded by plane surfaces, meeting at definite interfacial angles (§ 138)? To anyone with an inquiring mind, progress through any science is a constant effort to explain not only numberless astonishing facts but especially the laws that embrace so many facts.

So we find science attempting induction of a still higher order, by taking groups of related laws and fusing them into statements that are more general still. Concurrently, attempts are made to explain the laws, by making them appear as reasonable consequences of certain assumptions—commonly about the way in which things in general are put together or constructed out of other things. So we have the *Molecular Theory*, which assumes that the properties of materials in general are determined by invisibly small particles called molecules. Interwoven with this is the *Atomic Theory*, which asserts that molecules are frequently resolvable into still smaller particles called atoms; and that atoms, by being separated from one another and then recombined into other groupings, may create new sorts of molecules, thus transforming the original material into one or more new materials.

As chemistry made progress, the Atomic-Molecular Theory came to be supplemented by the *Ionic Theory*, which attempted to explain the laws of conductivity in solutions by assuming that molecules sometimes carry electric charges. Then, with the twentieth century, came the *Electronic Theory*, to explain how ions get their charges, why metals conduct electricity, what really happens in oxidation and reduction, why equal quantities of electricity are needed to deposit a gram-equivalent of any element (§ 523), and numerous other facts and laws. The *Quantum Theory of Radiation* and the *Wave-Mechanics Theory* of Atomic Structure explain still further facts. Doubtless we shall soon have a successful *Nuclear Theory*, to explain why the nuclei of radioactive atoms are unstable, and why numerous recently studied nuclear transformations (§ 584) give the products that they do.

599. A Complex but Self-Consistent Universe

As theory joins theory in the development of science, natural phenomena seem to become ever more and more complex. The universe is no very simple affair, however simple the laws that we deduce to correlate phenomena that are carefully selected and idealized for the express purpose of giving simple form to the laws. But all the theories of science are interwoven. The Atomic-Molecular Theory would be

incomplete without the Ionic Theory, and this would leave too many laws and facts unexplained, were it not supplemented by the Electronic Theory.

So as we gradually penetrate the mysteries of the universe and realize more and more how very complex it is, we nevertheless glimpse its unity. The theories of every science carry over into other sciences, and each must stand the test of all the evidence that all the rest can bring to bear. The Planetesimal Theory concerning the origin of the earth must be found consistent with all the laws and principles of physics and chemistry, if it is to survive. The Theory of Evolution must undergo whatever tests may be applied by workers in the fields of embryology, paleontology, cytology, and biochemistry.

The far-flung universe thus stands revealed as the abode of law and order, from the electron and atom to the furthermost spiral nebulae; and the same great principles are manifested by the solid rocks beneath our feet, the marvels of chemical change, the wonderful world of living things with which we are surrounded, and the messages that starlight brings from distant space and remote time.

600. Scientific Prediction

To the processes of induction or generalization just described science adds an inverse process—*deduction.* This begins with established principles and laws, illuminated as well as possible by general theories, and thence infers all sorts of detailed phenomena that might otherwise have remained unnoticed or unknown.

In this manner science gains the gift of prophecy. The properties of an element and of its simpler compounds are predicted in advance of their discovery, by deduction based on the Periodic Table. The properties of a new local anesthetic are anticipated with some degree of assurance, in advance of its synthesis, by deduction based on its structural formula. The strength of engineering structures and indeed all the operations of the engineering professions are based on predictions obtained by calculations derived from the principles of chemistry and physics. Eclipses are forecast by calculations based on the law of gravitation. The general effect of crossing different breeds of plants or animals is foretold on the basis of Mendel's Law of Inheritance. *As science gains in power it gains in ability to prophesy.* We may measure its command over any field in the degree of certainty with which its predictions come true.

The predictions of science are given with some hesitation whenever it is realized that data are scanty or generalizations not well tested.

We then expect a large proportion of cases in which its predictions fail to be verified. But science learns from its errors and gains power as it corrects its mistakes. If it ventures the hypothesis that crystal form is chiefly determined by the relative sizes of the atoms or ions of which a crystal is constructed (§ 144), it soon discovers that the size which must be assigned to any given particle depends on the nature of the forces that act upon it and on their ability to flatten or distort the particle. So, gradually, the ability is developed to predict the crystalline form of a material from its chemical formula and eventually to predict, at least roughly, such properties as melting point, electrical conductivity, and elasticity.

The most accurate and reliable of the predictions of science are the result of mathematical calculations, based on laws that happen to be precise enough to be capable of mathematical expression. All the sciences, as they advance, must rely more and more on mathematics, the most keenly sharpened tool of science. This long ago passed the simple stage of algebra, in which measurable quantities of all sorts are represented by the letters of the Roman and Greek alphabets. Almost three centuries ago, in the hands of Newton and Leibnitz, it began to concern itself with rates of change and with the conclusions that may be drawn from observed rates of change with regard to the changing quantities themselves. This is one aspect of the calculus.

Today we have other varieties of mathematics, in great number, some of which the aspirant chemist must master, dealing with what the mathematician calls complex quantities, which are of value in the prediction of real phenomena but themselves evade all our attempts to visualize, and completely defy interpretation within the frame of ordinary space and time.

601. The Scientific Method

We have now disclosed some of the essentials of what has been called *the scientific method.* This is merely the method of straightforward thought. Francis Bacon perceived its essentials three hundred years ago:

1. To recognize a problem to be solved.
2. To devise and carry through a method for solving it.
3. To check the conclusion thus reached by independent tests, in the light of all the facts and principles that have already been established.
4. To give the conclusion an interpretation, in terms of facts, laws, or theories already known.

5. When uninterpreted facts have accumulated in great number, cautiously to propose new theories, never venturing any complicating theory until all simplifying ones have been proved inadequate.

More briefly, you must first be conscious of being at information's end, take one step more, make sure you are still on solid ground, then pause to look about you, and *think* about what you see. Science prefers to progress by this, the Baconian method; but when no guiding general principles are known it is not above resorting to the Edisonian method, which just tries everything. In its applications, science frequently outruns complete theoretical explanations. Were this not true we should have had no automobiles until we had learned more about the chemistry and physics of explosive combustion.

A tenet of science that is much misunderstood—truth for its own sake—means "truth for the sake of science." Science often best makes progress by proceeding from the simple to the complex. It often happens that discoveries that need to be made to clear the way for future progress are not themselves of immediate practical use. Science is like a mosaic pavement, into which successive fragments of truth must be fitted with regard to the beauty and completeness of the whole, without the least concern about the practical uses that might otherwise be made of the fragments individually.

602. Science as Self-Consistent Thinking

Because science advances by the method just described, hypotheses that are in active use as instruments of deduction constantly change their aspect as they harden into laws. Tentative conclusions may have to be abandoned; and every result is subjected, not merely to experimental tests, but also to examination to determine whether it is in complete harmony with every related fact and every accepted law. Science will not endure any shadow of inconsistency.

We may characterize science, then, not merely as systematic thinking, but as the art of *self-consistent thinking.* The body of science always includes ideas that have made every degree of progress from verdant hypothesis to thoroughly established laws. But these are always under fire. If they prove to be inconsistent with the body of other facts and laws, they are ruthlessly cast out.

Such tests grow more numerous and severe with every passing year, since the interconnections of truth with truth cross all the boundaries between the various sciences. An untested conclusion in physiology may be overwhelmed by the weight of evidence from physics

and chemistry. Science is constantly considering which of its details are certain and which merely probable.

It is this willingness of science to discard unfruitful ideas and retrace false steps that gives us confidence in the permanence of its results. It is the only *self-purifying* system of thought thus far invented.

603. Mental Processes in the Scientific Method

In applying the scientific method we need to invoke such mental processes as *classification* and *selection*, the *analysis* of complex phenomena into their component parts, the *synthesis* of disconnected facts or ideas into an interconnected whole, the *comparison* of related phenomena, and *reasoning by analogy*. All these mental processes may be applied in any problem that comes up in any science. All of them are carried on concurrently with experimental work that involves the use of scientific instruments, from simple meter stick and measuring flask to complex equipment for measuring the wavelength of light or for disrupting the nuclei of atoms.

A scientific worker must possess imagination. He must constantly seek new interconnections between ideas or phenomena that at first may seem quite unrelated. He must constantly imagine possible causes for things turning out as they do. Yet this must be disciplined imagination, which devises stern tests to be applied to itself with each step in advance, to distinguish between daydreams and reality. Were it not for this need for distinguishing fact from fancy, science might be regarded as a branch of creative literature. Science is really an expression of the artistic impulse. The man who devotes his days to scientific research finds the same sense of artistic satisfaction in proportion, balance, and growth toward perfection that the painter and sculptor do.

The spirit of science is furthermore in harmony with the finest ideals of character. For the scientific worker needs such qualities as patience, disinterestedness, earnestness, devotion, honesty, diligence, judgment, and system. He must be impartial, fair-minded, and devoid of prejudice. He must be bold in venturing into new fields, stout-hearted in defending his convictions, brave in admitting error. He must be tolerant and teachable, enthusiastic yet self-disciplined.

604. The Strength and Weakness of Science

We have implied that the chief strength of science is in its *disinterestedness*, made evident by its practice of subjecting each new conclusion to every possible test.

Nevertheless we may easily recognize the chief weakness of science. It is in beginning with a process of *selection.* We select and compare phenomena that seem to our human understanding to be related; and in so doing we may happen to ignore others that might alter or reverse our general conclusions. This is especially true when the phenomena to be studied are very complicated, as in the biological sciences and in medicine.

A second weakness is that insecure generalizations sometimes become so familiar and remain so long in use that they are mistakenly regarded as established truth. They then actually hinder progress, as when mistaken views concerning ionization tended to retard progress in understanding reactions in solution. But errors of that sort are sure to be detected, the more quickly the more workers throng the field of science, attacking every new and old problem from many different points of view.

605. Scientific Truth

We have seen that the body of science, at any given moment, always includes some results that are in process of being verified, and some provisional general principles that are slowly hardening into laws. In this respect it is like a living organism, which grows and enlarges its framework, meanwhile strengthening that framework by the hardening of cartilage into bone. But along with recently won probabilities there is a larger and more important collection of material which may fairly be regarded as established truth.

What, then, does science regard as well established? *Anything, indeed, that has been tested in many different ways and found consistent with all the details and principles of previous scientific truth.* The statement that Mars is inhabited is not acceptable as scientific truth, since we have not sufficient evidence to support it. The statement that certain diseases are caused by bacteria is scientific truth, since the supporting evidence is overwhelming, and since we do not run into inconsistencies in subscribing to this belief.

Of course it often happens that the conclusions of science are not subject to direct experimental test. Their admission or rejection then depends on circumstantial evidence. The existence of atoms and molecules is accepted as proved, because all sorts of independent evidence agree concerning their sizes, weights, and numbers. We are not troubled by the fact that we cannot hope to see them, for evidence of their existence is just as convincing as the evidence of a post collided with in the dark.

There are other instances in which direct tests of conclusions are made difficult because we cannot exclude complicating factors. Thus a remedy that cures ninety-nine patients may kill the hundredth one, because of complicating circumstances that could nót be foreseen. The science of medicine has to take that chance. It has to be satisfied with what might be called *statistical truth.* This merely consists in saying that we shall accept a proposition as being proved when the chances of its truth become overwhelmingly great. Actually, few would demand a probability of one hundred to one. A physician who could be sure that nineteen patients would be cured and hail him thereafter as a great healer would doubtless be content to have the twentieth denounce him as a quack.

606. The Competitors of Science

Science commands respect by the triumphs it has won and by its willingness to rectify its errors, and the consequent seeming sureness with which it makes progress. Scientific reasoning is so simple and straightforward that one might assume it to be the favorite mode of thought of civilized men. Yet it still has to compete with "wishful thinking," which finds it most easy to believe what it would like to believe; with superstition, which accepts beliefs of all sorts without any sort of examination at all; and with propaganda, which seeks deliberately to prejudice or deceive. We live in the midst of a world transformed by science, accepting all its comforts and advantages, yet our mental habits have much in common with the days of the Crusades. The spirit of the Middle Ages still survives.

Indeed, to the age-old superstitions of primitive mankind we have added a swarm of new cults and pseudo-sciences, from astrology to vibro-therapy, numbering adherents by the hundred thousand. People of presumed culture seem quite unashamed of credulity and superstition.

The human brain has obviously not yet evolved into an efficient engine of thought, but is prone to defraud and deceive itself by all manner of tricks and evasions, shrinking from unpleasant truths, embracing pleasant errors, avoiding all thought processes that seem difficult or laborious, running to extremes, building what it terms *systems of thought* for the purpose of avoiding thought, and retiring into speculation when crucial tests were more in order. It takes a real effort to *live* in the twentieth century, not merely move about in it.

607. Three Services Rendered by Training in Science

Whoever tries to think straightforwardly on any subject is sure to meet the difficulty that it is very hard to know what has been established as true, outside of one's own specialty. All sorts of untried hypotheses and false sciences are clamoring to be heard. Serious treatises on psychology, medicine, and electricity are on the library shelf, side by side with the books on telepathy, mental healing, and animal magnetism. Authoritative works on the chemistry of food are found next to others proclaiming the advantages of all sorts of weird special diets. No untrained reader can hope to distinguish the authoritative guide from the pretender.

The most important services that a course in any science can render are therefore three in number:

1. To pass in review the *experimental methods* by which this particular science discovers facts and distinguishes truth from error.
2. To reveal a few outstanding *laws* and *principles* which summarize what has already been discovered, together with a few *theories* which seem to explain the discoveries of the past and point the way to new discoveries.
3. To disclose a few *books* and *journals* to which an inquirer may turn for information concerning what has already been done or discovered, or a few *persons* to whom one might turn for advice in deciding what books are reliable or worth reading.

These ends seem important enough to justify training in several of the fundamental sciences, for everyone possessed of normal mental powers.

608. An Acid Test

In a world in which propaganda and deliberate intent to deceive seem more active than ever, a little training in science will put one on guard against the most brazen frauds. There is, moreover, a simple test by which any educated man or woman may judge whether an assertion is worthy of belief. He simply asks himself *how anyone would set out to prove it.*

If it is an assertion with regard to diet, for example, he immediately thinks of controlled experiments with guinea pigs, and later with human beings. If it concerns national policy, monopolies, or "social justice," he asks to have the terms defined, with something of the precision known to science, then wonders whether anyone has undertaken the impartial collection of statistical data, to prove or disprove the assertion. If no experimental proof seems possible, or if the terms

used have not been defined, nor statistical evidence collected and weighed, the idea may usually be swept aside as the offering of a demagogue or crank.

Yet only an educated man can apply this test. Plenty of statistical data have been collected in every field, unsuspected by the mere reader of newspapers; and the human mind has developed tools to work with that are unsuspected by the uneducated. Our acid test, after all, is only for the few to apply—for the lucky few who were born with sufficient mental motive force to make broad contacts with the work of other minds, in this and former generations.

609. Conclusion

So, in a world transformed by science, we may differ much in our ability to carry the methods of science into all the affairs of life. We must deal as best we can with other forces than science. Science is but a feeble means for motivating human life. It enlightens men, but fails to rouse them to deeds of heroism or self-sacrificing devotion. It creates wealth, but wealth may be misused. It dispels ignorance, banishes disease, and lightens all the tasks that humanity must perform, without informing us what we should do with leisure. It gives us command over the material resources of the earth, without assuring command over ourselves.

We have to admit that emotion is needed to rouse men to action. It is by the kindling flame of emotion that nations are incited to conquest or to follow the ways of peace; that persecutions are launched, or crusades undertaken, or reforms brought into being. All the weighty facts of science may be ignored or swept aside when men are determined to be blind to them.

The world would be happier today if the energizing emotions of humanity were under the control of intelligence. Science can only gradually mold public opinion through the pressure of established facts, in lands in which established facts are not too much hindered in becoming known. The most urgent problem in the world today seems not to be any unsolved problem of science, but rather that of applying the results and methods of science in all the world's affairs. To summon all the energies of the age and place intelligence in control—that is the need of the future.

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Consult cumulative indexes in library reference room for articles on general methods, philosophy, and purposes of science (also, recent issues of such magazines as *Science*, *Scientific Monthly*, etc.).

APPENDIX

A. METRIC UNITS

Rough Equivalents

(To be memorized)

Length

1 meter = 39 + in., or a little over a yard.

1 centimeter (cm) = $\frac{1}{100}$ meter = about 0.4 in. (This is the most important unit of length.)

1 millimeter (mm) = $\frac{1}{1000}$ meter = 0.1 cm = about $\frac{1}{25}$ in.

Weight or Mass

1 gram = about $\frac{1}{28}$ oz, avoirdupois. (A new American or Canadian 5-cent piece weighs 5 grams.)

1 milligram (mg) = $\frac{1}{1000}$ gram. (A postage stamp of the most common size weighs about 50 mg.)

1 kilogram (kg) = 1000 grams = roughly, 2.2 lb.

Volume or Capacity

1 liter = somewhat more than a U. S. quart.

1 milliliter (ml) = roughly $\frac{1}{30}$ of a U. S. fluid ounce. It is the volume occupied by 1 gram of water, weighed in a vacuum at 4°C. It was intended to be—and is, with a negligible error—the same as 1 cubic centimeter (cm^3 or cc).

CONVERSION FACTORS

	English to Metric	*Metric to English*
Length	1 in. = 2.540 cm	1 cm = 0.3937 in.
Area	1 sq in. = 6.4516 sq cm	1 sq cm = 0.1550 sq in.
Volume and capacity	1 cu in. = 16.386 cc	1 ml = 1 cc = 0.061 cu in. = 0.033814 U. S. fluid oz
	1 cu ft = 28.317 liters	1 liter = 0.26418 U. S. gal = 0.21998 Br. gal
	1 U. S. gal (liq) = 3.7853 liters	1 liter = 0.035316 cu ft
Mass	1 lb (avoir.) = 453.59 grams 1 oz (avoir.) = 28.35 grams	1 gram = 0.03527 oz (avoir.) 1 kg = 2.20462 lb (avoir.)

Density and concentration	1 lb/cu in. = 27.680 g/cc	1 g/cc = 0.03613 lb/cu in.
	1 lb/U. S. gal = 0.119826 g/cc	1 g/cc = 8.3452 lb/U. S. gal
		= 10.022 lb/Br. gal
Force	1 dyne = 1.01972 mg	
	1 gram = 980.665 dyne	
Pressure	1 lb/sq in. = 70.307 g/sq cm	1 g/sq cm = 0.01422 lb/sq in.
	1 lb/sq in. = 0.068046 atm	1 atm = 14.696 lb/sq in.
		= 2116.2 lb/sq ft
	1 atm = 1033.2 g/sq cm = 760 mm of Hg	
Energy, work, heat	1 ft-lb = 1.35582 joule (absolute)	1 joule (abs) = 0.73756 ft-lb
	1 Btu = 251.98 cal (mean)	1 cal (mean) = 0.0039685 Btu
	1 cal = 4.186 joule (abs)	
	1 joule = 10^7 erg = 0.23889 cal (mean)	
	1 cal (mean) = 4.181 joule (abs)	
	1 kilocalorie (kcal) = 1000 cal	
Power	1 ft-lb/sec = 0.0018182 U. S. hp	1 joule/sec = 1 watt
	= 1.35582 watt	= 0.001341 U.S.hp
	1 U. S. hp = 550 ft-lb/sec	1 watt = 0.73756 ft-lb/sec
	= 745.6 watt	
	= 745.6 joule/sec	

DEFINITIONS

Dyne—the metric unit of force; it is the force which, acting on a body of 1 gram mass, free to move, will increase or decrease the velocity of the body by 1 cm/sec, for each second that the force acts.

Erg—the work done by a force of 1 dyne, acting upon a body, while the body moves 1 cm in the direction in which the force is applied.

Calorie or **gram calorie** (more precisely called a 15° calorie)—the quantity of heat needed to raise the temperature of 1 gram of water from 14.5° to 15.5°C; or (nearly enough, for most purposes) the quantity of heat needed to heat 1 gram of water from any temperature to another that is 1 degree higher on the centigrade scale. A "defined calorie" is 4.1833 international joules.

Mean calorie—the $\frac{1}{100}$ part of the quantity of heat needed to raise the temperature of 1 gram water from 0° to 100°C.

British thermal unit (Btu)—the quantity of heat needed to raise the temperature of a pound of water from 39° to 40°F.

Joule—10^7 ergs. It is also the work performed when 1 coulomb of electricity is transferred through a circuit between two points having a difference of potential of 1 volt.

(For definitions of some important electrical terms and units refer to § 510.)

B. TEMPERATURE SCALES

The temperatures at which water freezes and boils, when the barometer stands at the standard height of 76 cm, are taken as standard temperatures or fixed points on the principal thermometric scales.

In the Fahrenheit scale (°F) the freezing point of water is arbitrarily taken as 32°, and its boiling point as 212°.

In the centigrade scale (°C) the same two points (freezing and boiling) are called 0° and 100°. "Room temperature" means about 20°C.

To convert Fahrenheit degrees into centigrade degrees subtract 32° and multiply by $\frac{5}{9}$. Thus 68°F = 20°C.

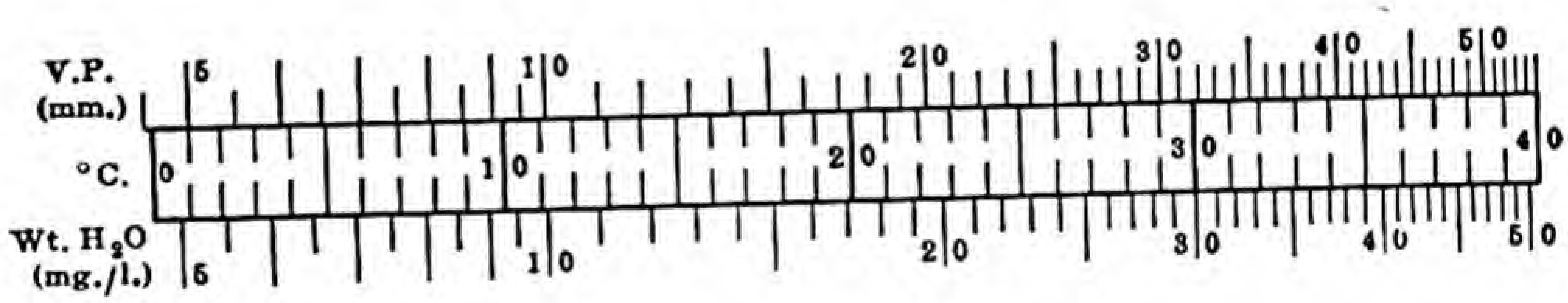
To convert centigrade degrees into Fahrenheit degrees, multiply by $\frac{9}{5}$ and add 32°. Thus 55°C = 131°F.

The absolute scale or Kelvin scale (§ 77) begins 273 degrees below the zero of the centigrade scale. To convert centigrade degrees to absolute degrees (°A or °K) add 273. To convert absolute degrees to centigrade degrees subtract 273.

C. VAPOR PRESSURE OF WATER

Correcting the Barometer for Vapor Pressure of Water

The middle scale in this chart gives temperatures on the centigrade scale. The upper scale shows the vapor pressure of water at each temperature, and the lower scale the number of milligrams of water in 1 liter of saturated air.



When gases are collected over water some of the water evaporates into the space occupied by the gas, intermingles with the gas, and relieves the gas of a part of the pressure that it would otherwise have to bear. To find the pressure actually borne by the gas subtract the vapor pressure of water at that temperature from the total pressure. Thus the vapor pressure of water, read from the chart at 20°C, is 17 mm. If the barometer then reads 720 mm the actual pressure on a gas that has been collected over water is 720 − 17 = 703 mm. This operation is sometimes called "correcting the barometer for the vapor pressure of water (aqueous tension)."

The "relative humidity" of air is the ratio of the weight of moisture actually contained in it to the weight contained in an equal volume of fully saturated air at that temperature. If the vapor pressure of the water vapor in the air is known, the relative number of moles of water vapor, in comparison with moles of air, is given by Dalton's Law (§ 118). From this the weight of the water vapor may be found.

D. PROPERTIES OF SOME COMMON GASES

Gases Difficult to Liquefy

	Melting Point	Boiling Point	Critical Temperature	Critical Pressure	Chief Chemical Characteristics
Argon, A	−188	−186.1	−117.4	52.9	Completely inert
Helium, He	−272	−271	−268	2.3	Completely inert
Hydrogen, H_2	−259	−252.8	−234.5	20	Reducing agent at high temperatures
Methane, CH_4	−184	−164	− 95.5	50	Combustible
Nitrogen, N_2	−210.5	−195	−146	33	Inert, except at high temperatures
Oxygen, O_2	−218	−182.7	−118	50	Unites directly with metals and non-metals
Carbon monoxide, CO	−207	−190	−141.1	35.9	Poisonous; combustible

Gases Easy to Liquefy

	Melting Point	Boiling Point	Critical Temperature	Critical Pressure	Chief Chemical Characteristics
Acetylene, C_2H_2	− 81	− 85	36.5	61.6	Unsaturated (§ 457); combustible
Ammonia, NH_3	− 77	− 38.5	130	115	Unites directly with water and acids; decomposed at a red heat
Carbon dioxide, CO_2	− 57	− 79	31.1	73	Acid-forming; reduced by hot carbon to CO
Chlorine, Cl_2	−101.5	− 34.6	146	93.5	Unites directly with metals and non-metals; oxidizing agent
Ethane, C_2H_6	−172	− 86	34	50.2	
Ethylene, C_2H_4	−169	−102.7	+ 10	51.7	Unsaturated; combustible; useful in anesthesia
Hydrogen chloride, HCl	−112.5	− 83.1	52.3	86	Extremely soluble in water; solution has properties of an active acid
Hydrogen sulfide, H_2S	− 85.5	− 61.8	100	88.7	Reducing agent; inactive acid; precipitant; decomposed when heated
Nitrogen dioxide, NO_2	− 9.6	21.6	171.2	147	Oxidizing agent
Nitrous oxide, N_2O	−102.4	− 89.4	38.8	77.5	Supports combustion; useful in anesthesia
Propane, C_3H_8	−190	− 42	95.6	43	Easily liquefied fuel gas
Sulfur dioxide, SO_2	− 72.7	− 10	155.4	78.9	Acid-forming; reducing agent; bleaching agent

E. OPERATIONS WITH VERY LARGE AND VERY SMALL NUMBERS

Very large and very small numbers are best expressed in powers of ten. Thus 10^8 means a 1, followed by eight zeros; namely, one hundred million; and 10^{-8} means a 1 in the eighth decimal place, preceded by zeros. Observe also that $10^0 = 1$.

In multiplying such numbers, add exponents. Thus 2.3×10^7, multiplied by 5×10^{-15}, is 11.5×10^{-8} or 1.15×10^{-7}.

In dividing, subtract exponents. Thus 27×10^{18} divided by 3×10^6 is 9×10^{12}.

In extracting square root, the number is most conveniently first adjusted so that the exponent is an even number. Thus 2.74×10^7 becomes 27.4×10^6. (Notice that the 2.74 of the original number has here been multiplied by 10, and the 10^7 has been divided by 10, hence the product remains unchanged.) The exponent is now divisible by two. Divide the exponent by 2, in taking the square root. Thus the square root of 27.4×10^6 is $5.2+ \times 10^3$.

In extracting cube root adjust the number so that the exponent is a multiple of 3. Thus 2.74×10^{-8} becomes 27.4×10^{-9}. The 2.74 or the original number has here been multiplied by 10 and the 10^{-8} has been divided by 10, hence the product remains unchanged. The exponent is now a multiple of 3. Divide the exponent by 3, in taking the cube root. Thus the cube root of 27.4×10^{-9} is 3.015×10^{-3}.

F. BALANCING EQUATIONS

Simplest cases, §§ 46, 47.
Ion-electron method, for oxidation-reduction equations, §§ 262, 264, 265.
Valence state equations, §§ 266, 312, 380.

G. NUMERAL PREFIXES FROM LATIN AND GREEK

Use either of two different sets of numeral prefixes, in most applications. Never use a mixture of both. The Greek forms are tending to be preferred in naming *compounds*, and the Latin ones in a few words of Latin origin, as in indicating *reaction mechanism*, § 326, or *valence*. As prefixes in chemical words, Latin and Greek numerals take the following forms:

	1	2	3	4	5	6	7	8
Latin:	Uni-	bi-	ter- or tri-	quadri-	quinque-	sexa-	septa-	octa-
Greek:	Mono-	di-	tri-	tetra-	penta-	hexa-	hepta-	octa-

Also commonly used are the fractional prefixes:

hemi-	deci-	centi-	milli-	micro-
$\frac{1}{2}$	$\frac{1}{10}$	$\frac{1}{100}$	$\frac{1}{1000}$	$\frac{1}{1,000,000}$

For a survey of Latin and Greek roots contributing to chemical words see *J. Chem Educ.* **17**, 63–6 (1940).

H. DIMENSIONS

By the *dimensions* of any quantity we mean a statement of the manner in which certain simpler quantities (usually *distance*, *mass*, and *time*) are used in defining the given quantity. Thus an *area* is found by multiplying a length by a length, hence is said to have the dimensions of length squared or $[l^2]$, using brackets to stand for the word "dimensions." *Volume* is obtained by multiplying three lengths together, hence has the dimensions $[l^3]$.

Density is defined as mass per unit volume, hence must have the dimensions $[m/l^3]$. *Velocity* is defined as distance traversed in unit time, hence has the dimensions $[l/t]$. *Acceleration* is change of velocity in unit time, hence has the dimensions $[\text{vel.}/t] = [l/t^2]$.

Force is measured by the product of mass by acceleration (see textbooks of physics), hence has the dimensions $[m \times \text{acc.}] = [ml/t^2]$, otherwise written $[mlt^{-2}]$. *Work* is given by the product of a force by a distance, hence has the dimensions $[fl] = [ml^2/t^2]$, otherwise written $[ml^2t^{-2}]$. *Pressure* is defined as force per unit area, hence has the dimensions $[f/l^2] = [m/lt^2]$, otherwise written $[ml^{-1}t^{-2}]$.

Dimensions have three chief uses:

1. To help one determine what factor must be used in converting quantities from metric to English units, or conversely. Thus, if *pressure*, given in pounds per square foot, is to be converted into grams per square centimeter, we recall that pressure has the dimensions $[f/l^2]$. So the conversion factor needed is found by taking the factor that converts pounds (force) into grams and dividing it by the square of the factor that converts feet into centimeters.

2. Occasionally, to detect errors in algebraical equations. Quantities added or subtracted in an equation must all have the same dimensions, which must be the dimensions of whatever appears on the other side of the equation.

3. To suggest how to solve problems. (This is the use that students will most frequently make of dimensions.) For example, § 107 suggests that PV represents work. To prove it, take the product of the dimensions of P and V and find that the result has the dimensions of work.

$$\left[\frac{m}{lt^2}\right] \times [l^3] = \left[\frac{ml^2}{t^2}\right] = \text{Work}$$

So we see that the *volume* (in cubic feet) of the cylinder of an automotive engine, when multiplied by the average *pressure* (pounds per square foot) which the expanding hot gases exert during the "power stroke," gives the total work done, in *foot-pounds*, for each stroke.

As a final example, how may one combine *density*, *velocity*, *area*, and *time* in order to get *mass?* Recall the dimensions of the first four quantities mentioned and you will see that they must be multiplied to give the other quantity. In the metric system:

$$[\text{g/cm}^3] \times [\text{cm/sec}] \times [\text{cm}^2] \times [\text{sec}] = [\text{grams}]$$

Observe that cm and sec cancel out. So, if we multiply the density of a liquid being delivered through a pipe by its velocity in the pipe, then by the cross-sectional area of the pipe, and by the total time during which the liquid flows, we shall have the total mass or weight of the liquid delivered in that time.

I. IONIZATION CONSTANTS

Ionization Constants of Acids

Acid	Formula	K_a	pK_a	Temp. °C
Acetic	$HC_2H_3O_2$	1.86×10^{-5}	4.73	25
Benzoic	$HC_7H_5O_2$	6.6×10^{-5}	4.18	25
Boric	H_3BO_3	6.4×10^{-10}	9.19	25
Carbonic	H_2CO_3	3×10^{-7}	6.52	18
"	" (2d H)	6×10^{-11}	10.22	25
Hydrocyanic	HCN	7.2×10^{-10}	9.14	25
Hydrosulfuric	H_2S	9.1×10^{-8}	7.04	25
"	" (2d H)	1.2×10^{-15}	14.92	25
Hypochlorous	HClO	3.7×10^{-8}	7.43	17
Lactic	$HC_3H_5O_3$	1.55×10^{-4}	3.81	25
Nitrous	HNO_2	4×10^{-4}	3.40	18
Oxalic	$H_2C_2O_4$	3.8×10^{-2}	1.42	25
"	" (2d H)	4.9×10^{-5}	4.31	25
Phosphoric	H_3PO_4	1.1×10^{-2}	1.96	18
"	" (2d H)	2×10^{-7}	6.70	18
"	" (3d H)	3.6×10^{-13}	12.44	18
Sulfuric	H_2SO_4	4×10^{-1}(?)	0.40	25
"	" (2d H)	1.9×10^{-2}	1.72	18
Sulfurous	H_2SO_3	1.7×10^{-2}	1.77	25
"	" (2d H)	5×10^{-6}	5.30	25
Water (solvent)	H_2O	10^{-14}	14.00	25

Ionization Constants of Bases

Base	Formula	K_b	pK_b	Temp. °C
Acetamide	CH_3CONH_2	3.1×10^{-15}	14.51	25
Ammonium hydroxide	NH_4OH	1.8×10^{-5}	4.74	25
Aniline	$C_6H_5 \cdot NH_2$	4.6×10^{-10}	9.34	25
Arsenious oxide	As_2O_3	1.1×10^{-14}	13.96	25
Ethylamine	$(C_2H_5)_2NH$	5.6×10^{-4}	3.25	25
Pyridine	C_5H_5N	2.3×10^{-9}	8.74	25
Quinoline	C_9H_7N	1.0×10^{-9}	9.00	25
Thiourea	$CS(NH_2)_2$	1.1×10^{-15}	14.96	25
Urea	$CO(NH_2)_2$	1.5×10^{-14}	13.82	25
Water (solvent)	H_2O	10^{-14}	14.00	25
Zinc hydroxide	$Zn(OH)_2$	1.5×10^{-9}	8.82	25

Other data are given in a table on pp. 468, 469.

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(Starred entries are definitions.)

LOGARITHMS

To find the logarithm of 326.78:

In the table, opposite 32, in column 6, find	5132
In same row, proportional part 7, find	9
In same row, 1/10 of proportional part 8	1.1
Total, prefixing a decimal point,	.5142

This is the *mantissa*, or decimal part of the logarithm. It is *always positive.*

The *characteristic*, or whole number part of the logarithm, is—

1. *Positive for numbers greater than* 1. It is one less than the number of figures preceding the decimal point, e.g., 2 for 326.78 and 0 for 1.276.

2. *Negative for numbers less than* 1. It is (numerically) one more than the number of zeros immediately following the decimal point; thus $\bar{3}$ (namely -3) for 0.0027 and $\bar{1}$ for 0.27.

Thus the complete logarithm for 326.78 is 2.5142, and that for 0.0326 is $\bar{2}.5132$. This really means $-2 + 0.5132$, namely $-(1.4868)$.

To find the number corresponding to the logarithm 1.4129:

First consider the mantissa, 4129. The next lower mantissa in the table is that of 258. It is 4116, which needs 13 units more. In the same row, in the table of proportional parts, we find 12, in column 7, hence the fourth figure of the required number is 7. A 6, *in the next place* would be $1/10 \times 10 = 1$ unit more, making 13 units in all. The number sought is therefore 25.876, there being two figures preceding the decimal point, since the characteristic of the original logarithm is 1.

To multiply, add logarithms; to divide, subtract logarithms.

To extract square root, divide the complete logarithm of the number by 2. To extract cube root, divide the complete logarithm by 3. Check the final root, by a rough calculation. In extracting roots make the logarithm *all positive* or *all negative*, namely $\bar{2}.5132$ is written $-(1.4868)$. To extract the cube root we then divide by 3, thus obtaining $-(0.4956) = \bar{1}.5044$.

The *cologarithm* of a number is found by subtracting each figure of the logarithm from 9, except the last figure, which is subtracted from 10; then append -10.

Number	*Logarithm*	*Cologarithm*
326.78	2.5142	$7.4858 - 10 = \bar{3}.4858$

In a series of consecutive multiplications and divisions, use cologarithms for the divisions. *Add the cologarithm of each divisor instead of subtracting its logarithm.* Thus find $578 \times \frac{273}{298} \times \frac{746}{760}$:

$$
\begin{aligned}
\log 578 &= 2.7619 \\
\log 273 &= 2.4362 \\
\log 746 &= 2.8727 \\
\log 298 = 2.4742 \qquad \operatorname{colog} 298 &= 7.5258 - 10 \\
\log 760 = 2.8808 \qquad \operatorname{colog} 760 &= 7.1192 - 10 \\
\hline
& 22.7158 - 20 = 2.7158
\end{aligned}
$$

The result sought is 519.7

Natural Numbers.	0	1	2	3	4	5	6	7	8	9	Proportional Parts. 1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

Natural Numbers.	0	1	2	3	4	5	6	7	8	9	Proportional Parts. 1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

SOLUBILITY OF BASES AND SALTS IN WATER AT 18° C.

	Li	Na	K	Mg	Ca	Sr	Ba	Fe''	Fe'''	Cu''	Zn	Pb	Ag	Hg'	Hg''
F	0.27* 0.1042	4.4 1.048	92.3 15.89—2 aq.	0.0076** 0.0014	0.0016 0.0$_3$205	0.012* 0.0$_3$93	0.163* 0.0093	*			1.6 0.155—4 aq.	0.0641* 0.0026	185 14.32	Decomp.	Decomp.
Cl	77.0 18.16	35.9 6.14	33.4 4.48	54.1 5.68—6 aq.	72.5 6.54—6 aq.	52.8 3.33—6 aq.	35.2 1.69—2 aq.	41.5 3.27—4 aq.	89.8 2.76—12 aq.	75.6 5.62—2 aq.	362 26.54—1½ aq.	0.914* 0.0329	0.0$_3$15** 0.0$_4$11	0.0$_3$2** 0.0$_5$43	7.39 0.273
Br	174.0 20.02	89.0 8.65—2 aq.	64.1 5.38	96.1 5.21—6 aq.	141 7.05—6 aq.	98 3.96—6 aq.	103 3.46—2 aq.	53.5 2.48—6 aq.	s. —6 aq.	v.s. —4 aq.	441 19.59—2 aq.	0.804* 0.0219	0.0$_5$85** 0.0$_6$45	0.0$_5$4** 0.0$_7$7	0.4 0.0111
I	163.0 12.17	176.7 11.79—2 aq.	142.6 8.59	148 5.32—8 aq.	203 6.91—6 aq.	176 5.16—6 aq.	195	s.			432 13.55	0.066 0.0014	0.0$_6$3** 0.0$_7$13	0.0$_7$2 0.0$_9$31	**
ClO_3	213.5 23.6	97.0 9.11	6.7 0.546	130 6.80—6 aq.	177.8 8.59—2 aq.	175.0 6.88	35.5 1.166—1 aq.	s.	s.	164 7.12—4 aq.	198.8 8.55—4 aq.	151.3 4.05—1 aq.	10? 0.52	**	Decomp.
BrO_3	153.7 11.4	34.0 2.25	6.5 0.389	·	85 2.87—1 aq.	33 0.95—1 aq.	0.61 0.0155—1 aq.	s.	57.5	s.	58? 1.8—6 aq.	1.34 0.029	0.144* 0.0061	Decomp.	16
IO_3	80.3 4.41	8.5 0.429	7.5 0.350	8.22 0.22—4 aq.	0.26* 0.0067—6 aq.	0.026* 0.0$_3$60	0.021* 0.0$_4$43—1 aq.	*	*	0.121* 0.0033	0.9* 0.022	0.0019** 0.0$_4$34	0.004** 0.0$_3$14	**	**
NO_3	70.3 10.18—3 aq.	86.0 10.11	29.6 2.93	73.2 4.94—6 aq.	121.2 7.39—4 aq.	67.6 3.20—4 aq.	8.8 0.336	46.5 (24°) 2.58—9 aq.	s.	120 6.40—6 aq.	115.1 6.08—6 aq.	50.7 1.532	204 12.0	Decomp.	v.s.
SO_4	34.3 3.12—1 aq.	16.8 1.182—10 aq.	10.73 0.616	34.6 2.88—7 aq.	0.202* 0.015—2 aq.	0.0114** 0.0$_3$62	0.0$_3$23** 0.0$_5$99	26.4 1.74—7 aq.	*	19.9 1.25—5 aq.	53.0 3.28—7 aq.	0.0041** 0.0$_3$14	0.775 0.0248	0.06 0.0012	Decomp.
CrO_4	110.9 8.54—2 aq.	77.5 4.78—6 aq.	62.8 3.23	72.3 5.15—7 aq.	2.34 0.150	0.12* 0.0059	0.0$_3$38** 0.0$_4$15	0.022* 0.0012—2 aq.		**	**	0.0$_4$2** 0.0$_6$62	0.0025** 0.0$_4$75	*	Decomp.
C_2O_4	6.24 (25°) 0.612	3.5 0.261	37.7 (25°) 2.27—1 aq.	0.03* 0.0027—2 aq.	0.0$_3$56** 0.0$_4$44	0.0045** 0.0$_3$26	0.0089 0.0$_3$40—2 aq.		**	**	0.0$_3$64** 0.0$_4$42—2 aq.	0.0$_3$15** 0.0$_5$51	0.0035 0.0$_3$12	**	
CO_3	1.35 0.1823	19.5 1.840—10 aq.	111.5 8.08	0.095* 0.0113—3 aq.	0.0013** 0.0$_3$13	0.001** 0.0$_4$68	0.0022** 0.0$_3$11	**	Decomp.	**	0.001** 0.0$_4$81	0.0$_3$11** 0.0$_5$41	0.003** 0.0$_3$11	**	**
$C_2H_3O_2$	v.s. —2 aq.	47 5.73—3 aq.	245 25.0	v.s. —4 aq.	35.0 2.21—2 aq.	s.	69.7 2.73—3 aq.	s.	(basic) 0.023* 0.0012	7.2 0.396—1 aq.	40 (25°) 3.21—2 aq.	50 (25°) 1.538—3 aq.	1.005 0.0602	0.75 (13°) 0.029*	
OH	12.8 5.34—1 aq.	107.5 26.9—1 aq.	110 19.6—2 aq.	0.0$_3$84 0.0$_3$15	0.167 0.023	0.78 0.063—8 aq.	3.58 0.210—8 aq.	0.0$_3$67 0.0$_4$8	**	**	0.0$_3$56** 0.0$_4$56	0.0155* 0.0$_3$64	0.0022** 0.0$_3$18	**	
PO_4	**	19.6 1.18—12 aq.	v.s.	*	**	**	*	**	**	** —3 aq.	** —4 aq.	**	0.0064** 0.0$_4$13	**	**

See general statement of solubilities in § 141.

The upper number gives the number of grams of solute (calculated as anhydrous) that will dissolve in 100 g. of water at 18° C. The lower number gives the number of moles of solute in 1000 g. of water. If the solid in equilibrium with the saturated solution is a definite hydrate (§§ 124, 139), the symbol aq., preceded by a figure, indicates the number of molecules of water of hydration.

The figures for the solubilities of slightly soluble substances have been abbreviated; thus, 0.0$_3$15 means 0.00015. A star means a slightly soluble substance—solubility less than about 1 g. in 100 g. of water. A double star means an "insoluble" substance—solubility less than about 0.01 g. in 100 g. of water. s. means soluble: v.s. means very soluble.

PERIODIC TABLE Mendeleev's form, brought down to date

Group:	1		2		3		4		5		6		7		8A or 0	8B		
Oxide:	R_2O		RO		R_2O_3		RO_2		R_2O_5		RO_3		R_2O_7			RO_4		
Hydride:	RH		RH_2		RH_3		RH_4		RH_3		RH_2		RH		Inert Gases	Transition Triads		
Series	A	B	A	B	B	A	B	A	B	A	B	A	B	A				
1	1 H 1.008														2 *He 4.00			
2	3 Li 6.94		4 Be 9.02			5 B 10.82		6 C 12.01		7 N 14.01		8 O 16.000		9 F 19.00	10 *Ne 20.18			
3	11 Na 23.00		12 Mg 24.32			13 Al 26.97		14 Si 28.06		15 P 30.98		16 S 32.06		17 Cl 35.46	18 *A 39.94			
4 →	19 K 39.10	29 Cu 63.57	20 Ca 40.08	30 Zn 65.38	21 *Sc 45.10	31 *Ga 69.72	22 Ti 47.90	32 *Ge 72.60	23 V 50.95	33 As 74.91	24 Cr 52.01	34 Se 78.96	25 Mn 54.93	35 Br 79 92	36 *Kr 83.7	26 Fe 55.85	27 Co 58.94	28 Ni 58.69
5 →	37 Rb 85.48	47 Ag 107.88	38 Sr 87.63	48 Cd 112.41	39 Y 88 92	49 In 114.76	40 Zr 91.22	50 Sn 118 70	41 Cb 92.91	51 Sb 121.76	42 Mo 95.95	52 Te 127.61	43 * ?	53 I 126.92	54 *Xe 131.3	44 Ru 101.7	45 Rh 102.91	46 Pd 106.7
6 →	55 Cs 132.91	79 Au 197.2	56 Ba 137.36	80 Hg 200.67	57-71 Rare Earths	81 Tl 204.39	72 *Hf 178.6	82 Pb 207.21	73 Ta 180.88	83 Bi 209.00	74 W 183.92	84 *Po —	75 *Re 186.31	85 ? —	86 *Rn 222	76 Os 190.2	77 Ir 193.1	78 Pt 195.23
7	87 * —		88 *Ra 226.05		89-96 Actinide Elements													

Arrows indicate rows occupied by the post-transition elements (those having inner electron shells complete)

Lanthanide Elements (Rare earth series) { 57 La, 58 Ce, 59 *Pr, 60 *Nd, 61 * ?, 62 *Sa, 63 *Eu, 64 *Gd, 65 Tb, 66 *Dy, 67 *Ho, 68 Er, 69 *Tm, 70 *Yb, 71 *Lu

Actinide Elements { 89 *Ac, 90 Th, 91 *Pa, 92 U, $\underbrace{\text{93 *Np, 94 *Pu, 95 *Am, 96 *Cm}}_{\text{Synthetic}}$

PERIODIC TABLE

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
0	1 H 1.0078 K 1																	2 He 4.002 K 2
(He)	3 Li 6.94 KL 2·1	4 Be 9.02 KL 2·2											5 B 10.82 KL 2·3	6 C 12.00 KL 2·4	7 N 14.008 KL 2·5	8 O 16.000 KL 2·6	9 F 19.00 KL 2·7	10 Ne 20.183 KL **2·8**
(Ne)	11 Na 22.997 KLM **2·8**·1	12 Mg 24.32 KLM **2·8**·2											13 Al 26.97 KLM **2·8**·3	14 Si 28.06 KLM **2·8**·4	15 P 31.02 KLM **2·8**·5	16 S 32.06 KLM **2·8**·6	17 Cl 35.457 KLM **2·8**·7	18 A 39.944 KLM **2·8·8**
(A) KL **2·8**	19 K 39.096 MN 8·1	20 Ca 40.08 MN 8·2	21 Sc 45.10 MN 9·2	22 Ti 47.90 MN 10·2	23 V 50.95 MN 11·2	24 Cr 52.01 MN 13·1	25 Mn 54.93 MN 13·2	26 Fe 55.84 MN 14·2	27 Co 58.94 MN 15·2	28 Ni 58.69 MN 16·2	29 Cu 63.57 MN **18**·1	30 Zn 65.38 MN **18**·2	31 Ga 69.72 MN **18**·3	32 Ge 72.60 MN **18**·4	33 As 74.91 MN **18**·5	34 Se 78.96 MN **18**·6	35 Br 79.916 MN **18**·7	36 Kr 83.7 MN **18·8**
(Kr) KLM **2·8·18**	37 Rb 85.44 NO 8·1	38 Sr 87.63 NO 8·2	39 Y 88.92 NO 9·2	40 Zr 91.22 NO 10·2	41 Cb 93.3 NO 12·1	42 Mo 96.0 NO 13·1	43 ? 99 ± NO 13·2	44 Ru 101.7 NO 15·1	45 Rh 102.91 NO 16·1	46 Pd 106.7 NO 18·0	47 Ag 107.880 NO 18·1	48 Cd 112.41 NO 18·2	49 In 114.76 NO 18·3	50 Sn 118.70 NO 18·4	51 Sb 121.76 NO 18·5	52 Te 127.61 NO 18·6	53 I 126.92 NO 18·7	54 Xe 131.3 NO 18·8
(Xe) KLM **2·8·18**	55 Cs 132.91 NOP 18·8·1	56 Ba 137.36 NOP 18·8·2	57–71 Rare Earth Metals	72 Hf 178.6 NOP **32**·10·2	73 Ta 181.4 NOP **32**·11·2	74 W 184.0 NOP **32**·12·2	75 Re 186.31 NOP* **32**·13·2	76 Os 191.5 NOP* **32**·14·2	77 Ir 193.1 NOP* **32**·17·0	78 Pt 195.23 NOP* **32**·17·1	79 Au 197.2 NOP **32**·18·1	80 Hg 200.61 NOP **32**·18·2	81 Tl 204.39 NOP **32**·18·3	82 Pb 207.22 NOP **32**·18·4	83 Bi 209.00 NOP **32**·18·5	84 Po 210 NOP **32**·18·6	85 ? NOP **32**·18·7	86 Rn 222 NOP **32·18·8**
(Rn) KLMN **2·8·18·32**	87 ? OPQ 18·8·1	88 Ra 225.97 OPQ 18·8·2	89–96 Actinide Metals															

Atomic Number →
Atomic Weight →
Electron Orbits →
Electrons

NON-METALS

The different thicknesses of the sloping lines represent different degrees of similarity between A-Groups and B-Groups. Thus IVA and IVB are very closely related, but 1A and 1B only slightly.

The scale at the bottom of the table gives the most important valences (valence numbers) for each element. A valence number in excess of +3 is usually shown only when the given element is in association with another (commonly oxygen); Mn, for example, in permanganate-ion, MnO_4^-, has a valence number of +7

LIGHT METALS

New electron-group begun

TRANSITION HEAVY METALS

HEAVY METALS

Next-inner electron-group built up to 18

Outer electron-group built up to 8

Figures in bold-faced type indicate completed electron-groups.

INERT GASES

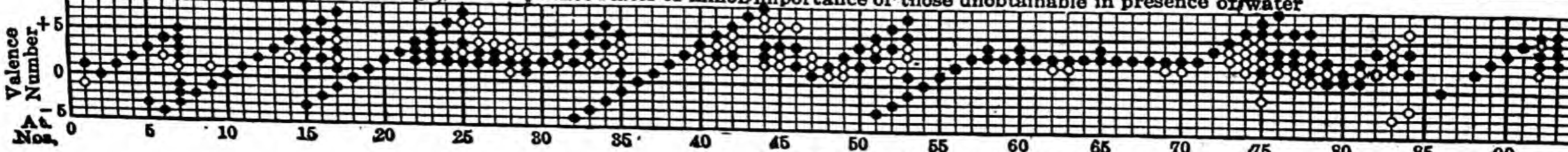
THE RARE EARTH METALS ARE:

57 La	58 Ce	59 Pr	60 Nd	61 ?	62 Sa	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP	NOP
18·9·2	19·9·2	20·9·2	22·8·2	23·8·2	24·8·2	25·8·2	25·9·2	26·9·2	28·8·2	29·8·2	30·8·2	31·8·2	32·8·2	32·9·2

THE ACTINIDE METALS ARE:

89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm
227 ±	232.12	231	238.14	Synthetic Elements			
OPQ	OPQ	OPQ	OPQ				
18·9·2	18·10·2	18·11·2	18·12·2				

Open circles represent valence states of minor importance or those unobtainable in presence of water



*Or with one less electron in outer group and one more in next inner

TO THE OWNER OF THIS BOOK

This book is intended for students whose training will include more than one year of chemistry. If they have had no previous work in the science, or only faulty preparation, they may omit the more advanced topics at the first reading, perhaps including some of them in a review, toward the end of the course.

In succeeding courses, this will serve as a reference textbook. Much may be forgotten, during the summer months, that will need to be reviewed, on short notice. There will be much more that advanced texts may obscure, by plunging too hurriedly into details. So retain your freshman text, to serve as an easy introduction to your later studies.